ATOMIC THEORY

FOR STUDENTS OF METALLURGY

WILLIAM HUME-ROTHERY,
M.A., D.Sc., F.R.S.

Royal Society Warren Research Fellow,
Lecturer in Metallurgical Chemistry,
University of Oxford

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GREEK ALPHABET.

A	α	Alpha	I	ι	Iota	P	ρ	Rho
B	β	Beta	K	κ	Kappa	Σ	σ	Sigma
Γ	γ	Gamma	Λ	λ	Lambda	T	τ	Tau
Δ	δ	Delta	M	μ	Mu	Υ	υ	Upsilon
E	ϵ	Epsilon	N	ν	Nu	Φ	ϕ	Phi
Z	ζ	Zeta	Ξ	ξ	Xi	X	χ	Chi
H	η	Eta	O	o	Omicron	Ψ	ψ	Psi
Θ	θ	Theta	Π	π	Pi	Ω	ω	Omega

CORRIGENDUM

It is regretted that a sentence on page 45 of the author's "The Structure of Metals and Alloys" and on page 7 of "Atomic Theory for Students of Metallurgy" is ambiguous or incorrect. The kX unit of length is larger than the true Angstrom unit. When a length is expressed in kX. units the *numerical value* is thus smaller than when the length is expressed in true Angstrom units, and all *values* in kX. units require multiplying by 1.00202 in order to give the values in true Angstrom units. We have thus: 1 Crystal Angstrom = 1 kX. unit = 1.00202×10^{-8}cm.

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INTRODUCTION.

In the last 25 years very great advances have been made in the theory of the structure and properties of metals and alloys. In this branch of science some of the underlying principles have been discovered empirically, but most of the quantitative theory is due to the great progress in Mathematical Physics which has resulted from the developments of the new quantum theory. Experience has shown that students of metallurgy are greatly interested in the new theoretical work, but are often quite unable to understand the papers or text-books written by mathematical physicists. This is due partly to the failure of the mathematician to appreciate the difficulties of the non-mathematical reader, and partly to the fact that most books assume a knowledge of subjects with which the metallurgical student is unfamiliar, although they are now included in the training of physicists, chemists, and crystallographers. This position is clearly unsatisfactory, and the present monograph has been written in the hope of providing a bridge by means of which the student of metallurgy may be led to an understanding of the general ideas on which the new theories are based. At the request of the Publication Committee of the Institute of Metals the monograph has been made reasonably self-contained, with the result that some of the subject-matter in Parts I, II, and III has already been treated in books of a reasonably elementary standard. It is hoped, however, that this repetition may be justified by the rearrangement of the material so as to form a general introduction to the theory of metals. The book is written primarily for the Honours Student in Metallurgy, and no attempt has been made to deal with mathematical technique. This method of approach means that equations have sometimes to be presented dogmatically, and it is hoped that this may be excused in view of the desirability of teaching the student not to be afraid of papers which contain numerous equations whose derivation he cannot hope to follow.

In dealing with the applications of the theory it has been thought better to concentrate mainly on the properties for which the theories have provided a reasonably straightforward explanation, and to avoid those whose interpretation is still in doubt. This means that the important property of plasticity has not been discussed, as it was felt that this subject would have led too far from the electronic theory with which the book is mainly concerned.

The manuscript was prepared before the announcement of the

methods for the utilization of atomic energy, and as these have not yet any direct metallurgical application, it has been decided to omit them entirely from the present monograph.

The author must express his gratitude for the great help he has received from many friends in the preparation of this monograph. Particular thanks are due to Professor N. F. Mott, F.R.S., and Dr. H. Fröhlich, who have read the whole of the manuscript, to Dr. R. Sack, who gave much useful help, and to Dr. C. A. Coulson who has given great assistance with the proof corrections. Professor R. Peierls and Dr. H. Jones have also shown great kindness in discussing some of the theoretical points. On the metallurgical side, Dr. A. H. Cottrell, Dr. J. A. Wheeler, and Dr. H. J. Axon have given valuable advice as to the requirements of the University student, whilst Dr. G. V. Raynor has given much help in reconciling the points of view of the metallurgist and the physicist. The author must also acknowledge the great help given by Mr. N. B. Vaughan (formerly Assistant Editor of the Institute of Metals) in connection with the preparation of the manuscript and diagrams. It need scarcely be said that the fact that the friends mentioned above have read the manuscript in no way commits them to the views expressed in the monograph.

W. H.-R.

The Inorganic Chemistry Laboratory,
The University Museum,
Oxford.

NOTE TO FIRST, REVISED, REPRINT

A reprint of this Monograph has been required unexpectedly soon, and the original printing has therefore been retained with the addition of an Appendix dealing with the exact formulation of the Uncertainty Principle of Heisenberg. A few additions have been made to the suggestions for further reading, and some corrections and modifications have also been introduced. The author will be grateful if readers will notify him of any errors or misprints which may be found in the text.

Oxford. W. H.-R.

6th February, 1947.

NOTE TO SECOND, REVISED, REPRINT

The Monograph is reprinted unchanged except for alterations on pp. 235–236 and 253–256, resulting from new work by Zener and Matyas.

Oxford, W. H.-R.

22nd November, 1947.

PART I.—THE GENERAL BACKGROUND.

Chapter I.—General Introduction.

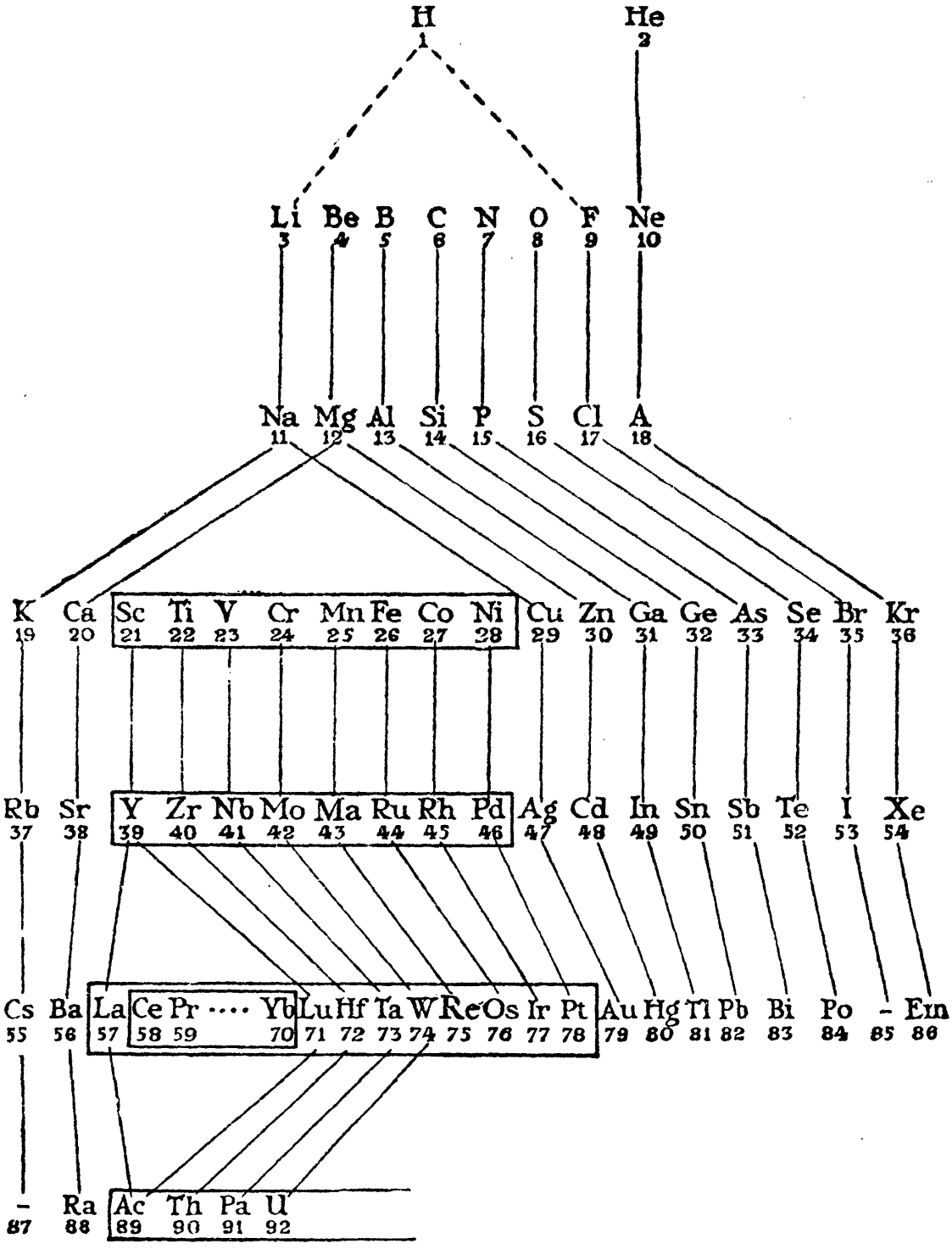
The modern theory of atomic structure is the result of work in chemistry, physics, and mathematics, extending over more than 150 years, and involving very great changes in the underlying ideas. We do not propose to deal here in detail with the historical development of the subject, but it may be of interest to point out some of the more prominent stages by which the present position has been reached.

The atomic theory of John Dalton provided the Science of Chemistry with a sound foundation, and its developments by the great chemists of the nineteenth century culminated in Mendeleev's Periodic Table of the Elements which appeared in 1869. This table, which is reproduced in a modified form on p. 2, showed that a periodic repetition of physical and chemical properties was observed if the elements were arranged in a definite order which, with a very few exceptions, was the order of increasing atomic weight. These developments of what may be called the simple atomic theory of chemistry clearly supported the view that matter consisted ultimately of atoms, which in ordinary chemical reactions were indestructible, but which could combine together to form molecules in accordance with the principles of valency. At the same time the growth of the Science of Electrochemistry, which began with the work of Davy and Faraday, suggested that electricity had some kind of an atomic structure, since the gram-molecular weights of the different ions were associated with small whole-number multiples of a definite electric charge. The periodicity revealed in Mendeleev's table suggested that the atoms themselves had structures, and that on passing down the Periodic Table, the changes in atomic structure involved the building up of a series of stable groups or units, so that each time a group was completed, the building up process began again.

The development of the Science of Chemistry led to the determination of the relative weights of the atoms of the different elements, and these are now expressed on a scale in which the atomic weight of oxygen is taken to be 16·000. On this scale the atomic weight of hydrogen is 1·0080, and the atomic weights at present accepted are given in Table I.

In the middle and latter half of the nineteenth century, the development of the kinetic theory of gases showed that many properties of

the gaseous state could be explained on the assumption that a gas consisted of an assembly of small particles, the average velocity of which increased with rise of temperature. These "particles" were



[Courtesy Clarendon Press.

Periodic Table of the Elements.

naturally identified with the molecules of chemistry, and several different lines of approach led to the conclusion that the number of molecules present in the gram-molecular weight of a substance was of

the order 10^{24}. Later and more perfect methods have shown that this number, which is known as *Avogadro's number*, is equal to $6{\cdot}0228 \times 10^{23}$. In the case of carbon monoxide, for example, the atomic weights are carbon = 12·010 and oxygen = 16·000, and consequently 28·010 g. of carbon monoxide contain $6{\cdot}0228 \times 10^{23}$ molecules of CO.

TABLE XII.—*International Atomic Weights*, 1941.

	Symbol.	At. No.	At. Wt.		Symbol.	At. No.	At. Wt.
Aluminium	Al	13	26·97	Neon	Ne	10	20·183
Antimony	Sb	51	121·76	Nickel	Ni	28	58·69
Argon	A	18	39·944	Niobium (Columbium)	Nb (Cb)	41	92·91
Arsenic	As	33	74·91	Nitrogen	N	7	14·008
Barium	Ba	56	137·36	Osmium	Os	76	190·2
Beryllium	Be	4	9·02	Oxygen	O	8	16·0000
Bismuth	Bi	83	209·00	Palladium	Pd	46	106·7
Boron	B	5	10·82	Phosphorus	P	15	30·98
Bromine	Br	35	79·916	Platinum	Pt	78	195·23
Cadmium	Cd	48	112·41	Potassium	K	19	39·096
Cæsium	Cs	55	132·91	Praseodymium	Pr	59	140·92
Calcium	Ca	20	40·08	Protoactinium	Pa	91	231
Carbon	C	6	12·010	Radium	Ra	88	226·05
Cerium	Ce	58	140·13	Radon	Rn	86	222
Chlorine	Cl	17	35·457	Rhenium	Re	75	186·31
Chromium	Cr	24	52·01	Rhodium	Rh	45	102·91
Cobalt	Co	27	58·94	Rubidium	Rb	37	85·48
Copper	Cu	29	63·57	Ruthenium	Ru	44	101·7
Dysprosium	Dy	66	162·46	Samarium	Sm	62	150·43
Erbium	Er	68	167·2	Scandium	Sc	21	45·10
Europium	Eu	63	152·0	Selenium	Se	34	78·96
Fluorine	F	9	19·00	Silicon	Si	14	28·06
Gadolinium	Gd	64	156·9	Silver	Ag	47	107·880
Gallium	Ga	31	69·72	Sodium	Na	11	22·997
Germanium	Ge	32	72·60	Strontium	Sr	38	87·63
Gold	Au	79	197·2	Sulphur	S	16	32·06
Hafnium	Hf	72	178·6	Tantalum	Ta	73	180·88
Helium	He	2	4·003	Tellurium	Te	52	127·61
Holmium	Ho	67	164·94	Terbium	Tb	65	159·2
Hydrogen	H	1	1·0080	Thallium	Tl	81	204·39
Indium	In	49	114·76	Thorium	Th	90	232·12
Iodine	I	53	126·92	Thulium	Tm	69	169·4
Iridium	Ir	77	193·1	Tin	Sn	50	118·70
Iron	Fe	26	55·85	Titanium	Ti	22	47·90
Krypton	Kr	36	83·7	Tungsten	W	74	183·92
Lanthanum	La	57	138·92	Uranium	U	92	238·07
Lead	Pb	82	207·21	Vanadium	V	23	50·95
Lithium	Li	3	6·940	Xenon	Xe	54	131·3
Lutecium	Lu	71	174·99	Ytterbium	Yb	70	173·04
Magnesium	Mg	12	24·32	Yttrium	Y	39	88·92
Manganese	Mn	25	54·93	Zinc	Zn	30	65·38
Mercury	Hg	80	200·61	Zirconium	Zr	40	91·22
Molybdenum	Mo	42	95·95				
Neodymium	Nd	60	144·27				

The determination of Avogadro's number led to an estimation of the actual as distinct from the relative weights of the atoms of the different elements, and this knowledge, when combined with the known densities of substances, suggested that the distances between atoms in solids were of the order 10^{-7}–10^{-8} cm. The subsequent development (1913–20) of crystal analysis by X-ray diffraction methods confirmed this experimentally, and in so far as the interatomic distances in crystals are a measure of the sizes of the atoms concerned, we now know that the values lie between 10^{-7} and 10^{-8} cm., and the interatomic distances in solid metals have been determined to a degree of accuracy which is often as high as 1 part in 50,000.

The periodicity shown in Mendeleev's table suggested clearly that atoms were not analogous to very minute billiard balls, but that they possessed definite inner structures. The modern theory of atomic structure is founded essentially on the experimental work at the end of the nineteenth century which led to the discovery of the electron. In this work it was shown that under appropriate conditions, such as electrical discharges in gases, high temperatures (thermionic emission), and strong electric fields, many substances could be made to emit " rays " which on passing through electric or magnetic fields behaved as though they consisted of very minute particles carrying charges of negative electricity. These experiments showed that although the velocities of the emitted electrons varied greatly with the experimental conditions, the mass m and charge e of the electrons were always the same, irrespective of the substance from which the electrons were produced. The values accepted at present for these constants are :

electronic mass, $m = 9{\cdot}1066 \times 10^{-28}$ g.
electronic charge, $e = 4{\cdot}8025 \times 10^{-10}$ electrostatic units.

The mass of the electron is thus about $\frac{1}{1840}$ that of a hydrogen atom, whilst its electric charge is the same as that on a univalent negative ion.* The development of the methods of mass spectroscopy by J. J. Thomson and F. W. Aston enabled the masses and charges of electrons and ions to be studied in detail, and this work showed that whilst both positive and negative ions existed, only negative electricity was associated with a mass as small as that of an electron.† This

* The charge on one gram-molecular weight of a univalent ion is called a faraday, and is equal to 96,487 absolute coulombs. The charge on one single ion is therefore $96{,}487 \div 6{\cdot}0228 \times 10^{23} = 1{\cdot}60203 \times 10^{-19}$ coulombs. Since 1 coulomb $= 2{\cdot}99776 \times 10^{9}$ electrostatic units, the charge on one ion is equal to $1{\cdot}60203 \times 2{\cdot}99776 \times 10^{-10} = 4{\cdot}8025 \times 10^{-10}$ e.s.u., which is the value given above for the electronic charge.

† We are here ignoring the latest developments of physics which have led to the discovery of positive electrons, since this has at present no application to metallurgy.

led naturally to the idea of an atom as consisting of a relatively heavy, positively charged body to which was attached a number of light, negatively charged electrons, and from this it was an easy step to the concept of a nuclear atom with negatively charged electrons revolving round a positively charged core. This concept of a nuclear atom received direct experimental confirmation from the investigations of Rutherford on the deflection of α-particles * when passing through matter, and his work led to the conclusion that an atom consisted of a minute positively charged nucleus, surrounded by a sufficient number of electrons to keep the atom as a whole neutral. The dimensions of the nucleus are of the order of 10^{-12} cm., and are thus very small compared with the distances between atoms in molecules or crystals (10^{-7}–10^{-8} cm.), though the positively charged nucleus contains almost the whole of the mass of the atom. The zone occupied by the surrounding electrons is of the order of 10^{-7}–10^{-8} cm., and is thus of the same magnitude as the interatomic distances in crystals. The positive charge on the nucleus is equal to $+ Ze$, where Z, the so-called *atomic number*, gives the position of the element in the Periodic Table. Since the atom as a whole is neutral, an atom of atomic number Z is surrounded by Z electrons, so that an atom of, say, copper of atomic number 29 contains a nucleus of charge $+ 29e$, surrounded by 29 electrons.

The development of the idea of a nuclear atom was accompanied by increasing evidence (1910–1930) that under some conditions the nuclei of atoms were not indestructible. The first discoveries were in connection with the phenomenon of radioactivity, where it was found that some of the heaviest elements underwent spontaneous disintegration into new elements, the process being accompanied by emission of positively charged α-particles, negatively charged electrons (β-rays), or very penetrating radiation (γ-rays). These investigations showed that certain elements, notably lead, could exist in forms which had different atomic weights, but were chemically indistinguishable. These discoveries, in the hands of Soddy, led to the concept of isotopes, this name being given to cases where an element could be shown to exist in the form of atoms which were of different atomic weights, but which had the same positive nuclear charge, so that they occupied the same position in the Periodic Table and were chemically indistinguishable.† Subsequent work showed that nearly all the elements met with on the

* α-Particles or α-rays are produced in some radioactive transformations and are doubly charged He^{++} ions, *i.e.*, helium atoms which have lost two electrons.

† Some chemical properties (*e.g.*, rates of reaction involving diffusion) may depend slightly on the weights of the atoms, but the differences are usually very small.

earth are really mixtures of isotopes; thus chlorine, of atomic weight 35·457, consists of a mixture of isotopes of atomic weights 35 and 37.

The conclusion reached was, therefore, that the characteristics of the atoms of elements are determined not by their atomic weights, but by the positive charges on their nuclei. The order of the elements in the Periodic Table is thus the order of increasing positive charge on the nucleus, each step in the table corresponding to an increased nuclear charge of $+e$. This order was first established conclusively by the X-ray spectroscopic investigations of Moseley (1912), whose work showed that in the few cases where the order of the elements in the Periodic Table was not the order of increasing atomic weight, the regular increase in nuclear charge was maintained. Thus, as can be seen from the table on p. 2, the order of the elements in the middle of the First Long Period is iron ⟶ cobalt ⟶ nickel, for which the nuclear charges are $+26e$, $+27e$, and $+28e$, respectively, whilst the atomic weights are 55·85, 58·94, and 58·69, so that cobalt and nickel are out of order as regards atomic weights, but in order as regards the nuclear charges.

Later experimental work on atomic structure has been concerned mainly with the structure of the nucleus, and although these developments lie outside the scope of the present book, they are of the greatest possible interest,* and have led to methods for the artificial breaking up of atomic nuclei. From what has been said above, it will be appreciated that the characteristics of an element depend essentially on the atomic number, *i.e.*, the number of positive charges on the nucleus, and it may be said that for the present the structure of the nucleus is in general unimportant for the study of metals and alloys, although the reader should note that the artificial production of radioactive isotopes of the more common elements has led to interesting methods for the study of such subjects as self-diffusion. In this work minute quantities of a radioactive isotope of an element such as silver are prepared and electroplated on to a piece of silver or of a silver alloy, and after an appropriate heat-treatment, the penetration of the radioactive isotope can be studied by measurements of the radioactivity of the metal at different depths.

From the above survey it will be evident that the general concept of a nuclear atom is the result of a long series of experiments of a widely varying nature, which indicate that the theory of atomic structure must involve the behaviour of electrons in the fields of force of a minute positively charged nucleus, and at distances from the nucleus which do

* The reader may consult a book such as "Introduction to Atomic Physics," by S. Tolansky. London: 1947. (Longmans, Green and Co.)

not exceed about 10^{-7} cm. Before describing the theory of the subject, we may consider briefly the units of measurement which are usually employed in connection with the structure of the atom.

The unit of length in most general use for atomic phenomena is the Angstrom unit (A.), which is equal to 10^{-8} cm. In X-ray crystallography an unfortunate position has grown up in which lattice spacings are given in what are usually called Angstrom units, though they are not exactly equal to 10^{-8} cm. These "crystal Angstroms" are actually based on the Siegbahn scale of X-units, an X-unit being defined so that the (200) spacing of calcite at 18° C. is equal to 3029·45 X-units. This definition made an X-unit as nearly as possible equal to 10^{-3} A. on the basis of the then known value of Avogadro's number. More accurate work has shown that a slight error was made, and the crystallographer's Angstrom unit requires multiplying by 1·00202 in order to convert it into the true Angstrom unit of 10^{-8} cm. The theory of atomic structure is not yet sufficiently advanced for this difference to be significant in any but a small minority of cases; nevertheless, the reader should bear it in mind and note that proposals have been made to use expressions such as "absolute Angstroms" to denote true Angstrom units of 10^{-8} cm., and expressions such as kX. or "crystal Angstroms" to denote the crystallographic unit which is equal to one thousand Siegbahn X-units.

For some purposes it is convenient to use the so-called "atomic unit of length," which is equal to 0·5292 A. As we shall see later (p. 14), the Bohr theory assumed that the one electron of the hydrogen atom could travel round the nucleus in a number of definite orbits or stationary states, and the atomic unit of length is the radius of the first Bohr orbit, and is equal to:

$$\frac{h^2}{4\pi^2 me^2},$$

where m and e are, respectively, the mass and charge of the electron, and h is Planck's Constant of Action, which is referred to later and which equals $6{\cdot}624 \times 10^{-27}$ erg-second. The atomic unit of length is employed because its use avoids the necessity for working out terms of the form $h^2/4\pi^2me^2$ which occur in some calculations.

For the measurement of energy, the results can be expressed either as the energy change per atom or as the energy change per gram atomic weight. When we are concerned with the individual atom or electron, the most convenient unit of energy is often the energy change involved when one electron falls through a potential difference of 1 volt. This quantity of energy is called an *electron volt*, and is equal to $1{\cdot}60203 \times$

10^{-12} erg. Avogadro's number states that there are $6{\cdot}0228 \times 10^{23}$ atoms in the gram atomic weight of an element, and hence an energy change of one electron volt per atom is equivalent to $1{\cdot}60203 \times 10^{-12} \times 6{\cdot}0228 \times 10^{23} = 9{\cdot}6487 \times 10^{11}$ ergs per gram atomic weight. Now 1 *joule* is equal to 10^7 ergs, and 1 *calorie* is equal to 4·1855 joules. Consequently an energy change of one electron volt per atom is equivalent to:

$$\frac{9{\cdot}6487 \times 10^{11}}{4{\cdot}1855 \times 10^{7}} = 23{\cdot}05 \times 10^{3} \text{ cal. per g.-atom}$$

$$= 23{\cdot}05 \text{ kg.-cal. per g.-atom.}$$

If, therefore, an electron in an atom or a molecule undergoes an energy change of 1 electron volt, the energy change involved is equivalent to that of a heat of transformation or reaction of 23·05 kg.-cal. per g.-atom, and this conversion factor should be borne in mind when trying to visualize the magnitudes involved when results are expressed in electron volts per atom. The latent heats of fusion of most metals lie in the range 0·5–10·0 kg.-cal. per gram atomic weight, so that a change of $\frac{1}{10}$ of an electron volt per atom is of the same order as a latent heat of fusion.

The energy changes involved in atomic transformations are also sometimes expressed in terms of wave numbers or frequencies. It is well known that the phenomena of interference effects led to the development of the wave theory of light, but that when absorption or emission processes occur, the facts can only be explained by means of the quantum theory. This theory was first advanced by Planck (1901) in order to explain the distribution of energy among the different wave-lengths of radiation emitted by hot bodies. According to the quantum theory (see p. 23), energy in the form of radiation can only be emitted in units or quanta of magnitude $E = h\nu$, where E is the energy, ν the frequency of the radiation, and h is Planck's constant referred to above. A beam of radiation of frequency ν is thus the result of an immense number of atomic processes each involving an energy change equal to $h\nu$. Conversely, if an atom gives rise to emission, as the result of an energy change E, it expels one quantum of radiation of frequency E/h. It can therefore be understood that in many cases where atomic processes result in the emission or absorption of radiation, it is convenient to express energy in terms of frequency by means of the relation $E = h\nu$. The velocity of light is usually denoted by the symbol c and is equal to $2{\cdot}99776 \times 10^{10}$ cm. per second, and since the velocity is equal to the product of the wave-length and the frequency, it follows that light of frequency ν, has a wave-length λ equal to c/ν, whilst the *wave number*, n,

or number of waves per cm.* is equal to ν/c. If, therefore, an atom undergoes a transition in which it emits one quantum of radiation of frequency ν, the energy change involved is $6{\cdot}624 \times 10^{-27}\ \nu$ ergs, and since the wave number n equals ν/c, the energy of a quantum of radiation of wave number n is $6{\cdot}624 \times 10^{-27} \times 2{\cdot}99776 \times 10^{10} \times n = 1{\cdot}986 \times 10^{-16} \times n$ ergs per atom. It is possible to use wave numbers as a measure of energy, and combination of the above factors will show that an energy change of y electron volts per atom is equivalent to a wave number $n = 8{\cdot}0665 \times 10^3 \times y$, and an energy change of wave number n is equivalent to $1{\cdot}2397 \times 10^{-4} \times n$ electron volts per atom. The wave-lengths of visible light are of the order of 3000–7000 A., so that an atomic transition which gives rise to visible light involves an energy change of the order of 30,000–15,000 cm.$^{-1}$ wave numbers or *ca.* 3·5–1·8 electron volts per atom. The wave-lengths of X-rays are of the order of 1 A., so that the atomic transitions involve energy changes about 1000 times as great as those which give rise to optical spectra.

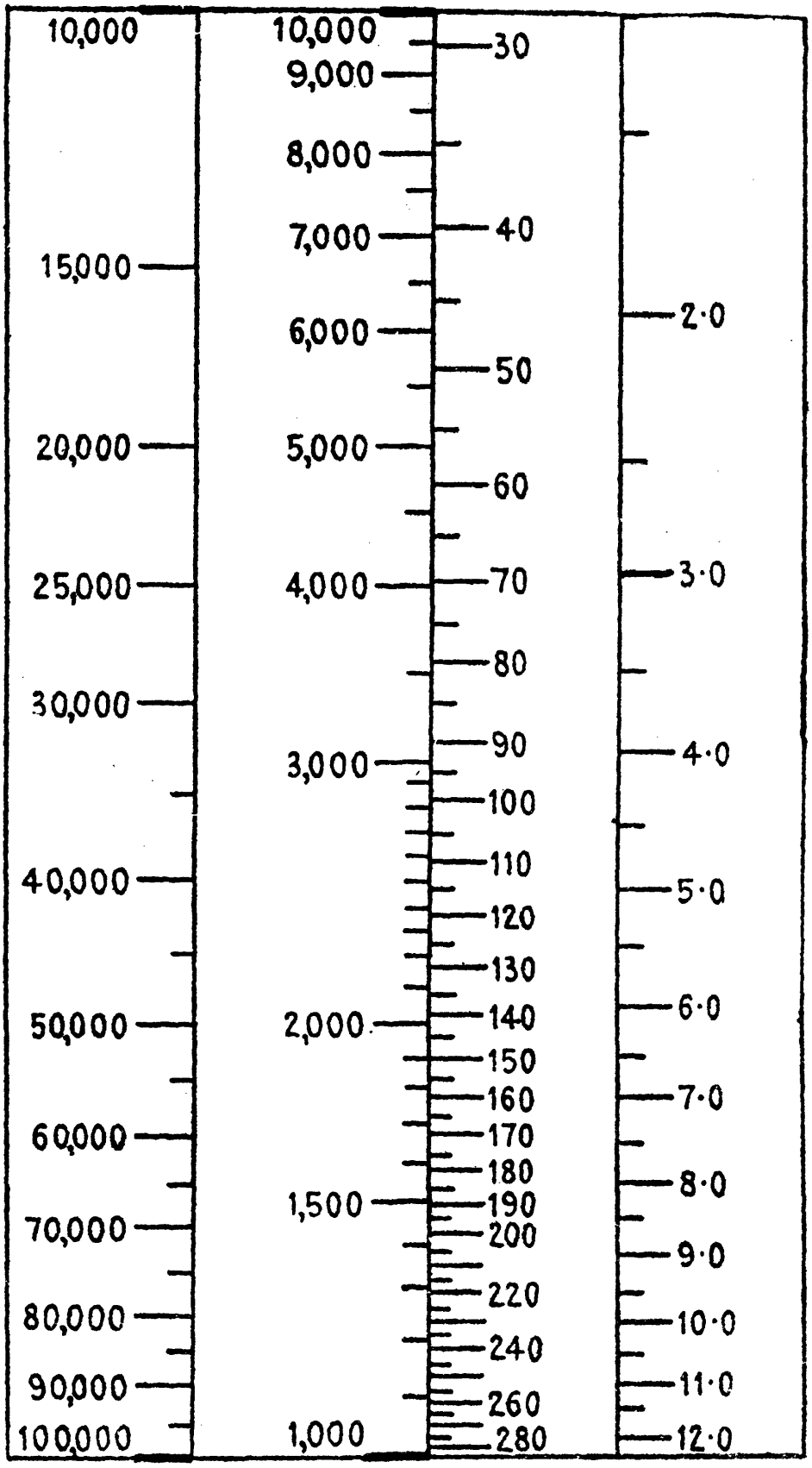
Fig. 1, which is taken from H. W. Thompson's " A Course of Chemical Spectroscopy " (Cambridge University Press) enables a comparison to be made between the above different units of energy over a certain range. The reader will also encounter energies measured in *Rydberg Units*, where 1 Rydberg = 13·59 e.v. This quantity of energy is equal to the first ionization potential of hydrogen, *i.e.*, the work required to remove an electron from a hydrogen atom in its normal or lowest energy state.

It is also useful to remember that in the equation for a perfect gas, $pv = R\theta$, the quantity $R\theta$ represents the energy of a gram-molecule of the gas at the absolute temperature θ; the constant R has the value 1·98647 cal. deg.$^{-1}$. The corresponding equation referred to a single molecule is $pv = k\theta$, where k is the so-called Boltzmann's constant, and equals $1{\cdot}38047 \times 10^{-16}$ erg deg.$^{-1}$. At room temperature θ is equal to approximately 300, so that $k\theta$ is of the order 4×10^{-14} ergs, *i.e.*, of the order of 3×10^{-2} e.v. This should be remembered when equations are encountered with terms of the form $e^{-\frac{E}{k\theta}}$, where E is the energy associated with some process.

Note on Physical Constants.

In the last 10 years slight changes have occurred in the accepted values of many of the physical constants used in atomic theory. These changes result from the discovery of errors in the oil-drop method of determining the electronic charge, e,

* It has, unfortunately, become a common practice to use the symbol ν both for the frequency and for the wave number which we have denoted by the symbol n, and the reader must be careful to distinguish between cases where ν means the real frequency and those where it means the wave number.



[*Courtesy Cambridge University Press.*

FIG. 1. (See p. 11 for legend.)

and also in some methods of determining the ratio h/e. The values given below are taken from the paper by R. T. Birge.* The position at the moment of writing is rather confusing, because Birge's values are now being used in most published papers, although they have not been officially recognized and are not to be found in the majority of text-books. In the present book it has not been possible to correct calculated values found in published papers and based on the older values of the physical constants. The changes are sometimes considerable: thus the old value of Avogadro's number was $6{\cdot}064 \times 10^{23}$, as compared with the present value of $6{\cdot}0228 \times 10^{23}$. Many of the constants are determined by methods which involve a knowledge of some of the other constants, and the reader who wishes to understand the details should consult the papers by Birge.

Velocity of Light, $c = 2{\cdot}99776 \times 10^{10}$ cm. sec.$^{-1}$.
1 Faraday, $F = 96{,}488$ absolute coulombs g.-equiv.$^{-1}$.
Avogadro's Number, $N = 6{\cdot}0228 \times 10^{23}$.
Electronic Charge, $e = 4{\cdot}8025 \times 10^{-10}$ abs. e.s.u.
Planck's Constant, $h = 6{\cdot}624 \times 10^{-27}$ erg sec.
Electronic Mass, $m = 9{\cdot}1066 \times 10^{-28}$ g.
Boltzmann's Constant (see p. 9), $k = 1{\cdot}38047 \times 10^{-16}$ erg deg.$^{-1}$.
Gas Constant per gram-molecule, $R = 1{\cdot}98647$ cal. deg.$^{-1}$.
Energy in ergs of 1 absolute volt electron (see p. 8) $= 1{\cdot}60203 \times 10^{-12}$ ergs.
Energy in kilocalories per gram-molecule for one absolute volt electron per molecule (see p. 8) = 23·052 kg.-cal.
Magnetic Moment of 1 Bohr Magneton $= 0{\cdot}9273 \times 10^{-20}$ erg gauss^{-1}.
Wave-length associated with one absolute volt (see p. 9) $= 12395 \times 10^{-8}$ cm. abs. volt.
Wave Number associated with one absolute volt (see p. 9), $n = 8067$ cm.$^{-1}$ absolute volt^{-1}.
1 Crystal Angstrom = 1 kX. unit $= 1{\cdot}00202 \times 10^{-8}$ cm.
Atomic Unit of Length, $a = 0{\cdot}5292 \times 10^{-8}$ cm.

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* *Rev. Modern Physics*, 1941, **13**, 233; another paper by the same author appears in "Reports on Progress in Physics," 1941, vol. 8, (Physical Society, London).

FIG. 1.—In this figure the right-hand scale is a logarithmic scale of electron volts. The next scale is the corresponding scale of kg.-cal./g.-molecule. On p. 8 we have explained that an energy change of 1 e.v./molecule is equivalent to 23·05 kg.- cal./g.-molecule, and it will be seen that 10 e.v. on the right-hand scale of Fig. 1 corresponds with 230·5 kg.-cal./g.-molecule on the adjacent scale. When an atom or molecule emits a quantum of radiation of frequency ν, the change in energy, E, of the atom is given by the relation:

$$E = h\nu = hc/\lambda,$$

where λ is the wave-length and c is the velocity of light. The third scale from the right shows the wave-lengths of the radiation corresponding to the energy changes of the first scale of e.v./molecule or of the second scale of kg.-cal./g.-molecule. Visible light has wave-lengths of the order of 3000–7000 A., and hence corresponds with energy changes of the order of 4–2 e.v. The left-hand scale is the corresponding scale of wave numbers, *i.e.*, number of waves/cm.

Chapter II.—The First Theory of the Hydrogen Atom.

In developing the theory of atomic structure, attention was naturally concentrated first on the hydrogen atom, since this consists of a single electron in motion round a nucleus with a single positive charge of $+ e$. In its simplest form, the first theory of the hydrogen atom assumed that the electron described a circular orbit round the nucleus, so that the inward attraction of the nucleus was balanced by the outward centrifugal force. Although the idea of a precise mechanical orbit has now been completely discarded, many of the general conclusions of this model are still valid and must be appreciated.

An electron describing a circular orbit round a positively charged nucleus of charge $+ e$, is attracted by a force equal to e^2/r^2. The electron possesses both potential and kinetic energies, and the potential energy, W, must be measured relatively to some arbitrary zero. For this purpose the zero of potential energy is assumed to be that of an electron at rest at an infinitely large distance from the nucleus. In a circular orbit of radius r, the potential energy is then *negative*, and equals $- e^2/r$.* The kinetic energy equals $\frac{1}{2}mu^2$, where u is the velocity. Since the centrifugal force, mu^2/r, is to be balanced by the attraction, we have :

$$\frac{mu^2}{r} = \frac{e^2}{r^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{I (1)}$$

so that the kinetic energy, K, is given by :

$$K = \tfrac{1}{2}mu^2 = \tfrac{1}{2}\frac{e^2}{r} \quad . \quad . \quad . \quad . \quad . \quad \text{I (2)}$$

and the total energy, E, is therefore :

E = potential energy + kinetic energy =

$$\frac{-e^2}{r} + \tfrac{1}{2}\frac{e^2}{r} = -\tfrac{1}{2}\frac{e^2}{r} \quad . \quad . \quad . \quad . \quad \text{I (3)}$$

The total energy is thus always negative † and becomes increasingly

* The negative sign of the potential energy is the result of the choice of zero and should give rise to no difficulty. If, for example, we consider a hill and a valley, and assume the potential energy of a stone in the valley to be zero, its potential energy on the top of the hill will be positive. But this procedure is clearly arbitrary, and we might equally well call the potential energy on the top of the hill zero, and in this case the potential energy in the valley would be negative.

† In some treatments it is customary to use some symbol, say Y, for the *negative* total energy, so that $Y = + \frac{1}{2}e^2/r$. It is this convention which often causes confusion as to whether large or small orbits have the greater total energy.

negative as the orbit becomes smaller. It is thus necessary to add energy if the electron is to be pushed out into a larger orbit. The kinetic energy equals $\frac{1}{2}e^2/r$, and hence the kinetic energy of an electron becomes smaller as the orbit becomes larger, and on comparing a large and a small orbit, we see that the larger orbit has the greater total energy and the greater potential energy, but the smaller kinetic energy. In so far as it is justifiable to think of "orbits" (see p. 44), these considerations apply to all the later theories.

Chapter III.—The Theory of Bohr.

The defect of the above classical theory was that it did not explain either the reason for the formation of sharp spectral lines, or for the stability of the atom. An electron moving in an orbit as described above would, on the basis of classical mechanics, continually approach the nucleus, with a steady emission of radiation of gradually changing frequency. The first step towards the solution of this problem was made by Bohr, whose original quantum theory of the atom involves two main assumptions :

(1) The electrons are assumed to revolve round the nucleus in definite orbits called *Stationary States*, and emission or absorption of radiation takes place by an electron jumping from one stationary state to another. When the electron jumps from an orbit of energy E_1 to one of energy E_2, the atom emits or absorbs a quantum of radiation of frequency ν, given by the Einstein relation :

$$E_1 - E_2 = h\nu, \quad . \quad . \quad . \quad . \quad . \quad \text{I (4)}$$

where h is the fundamental constant of Planck and equals $6{\cdot}624 \times 10^{-27}$ erg-second. Emission of radiation takes place if E_1 is greater than E_2, and absorption occurs if the atom gains energy during the transition.

(2) The only stationary states which are stable are assumed to be those for which the angular momentum is an integral multiple of $h/2\pi$. In this way an electronic orbit or state is associated with a whole number, the so-called *quantum number*. An electron can, for example, revolve in an orbit for which the angular momentum is $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi} \ldots$ or in general $\frac{nh}{2\pi}$, where n is the quantum number of the orbit. In a simple circular orbit, the angular momentum equals mur, so that the condition for quantization may be written :

$$mur = \frac{nh}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{I (5)}$$

This condition is an arbitrary postulate of the theory, and when combined with the relations given above leads to the expression :

$$E = -\frac{2\pi^2 me^4}{h^2} \times \frac{1}{n^2} \quad . \quad . \quad . \quad . \quad . \quad \text{I (6)}$$

The negative energies of the orbits are thus proportional to the inverse squares of whole numbers. From equation I (4), the frequency of the

quantum of energy emitted when an electron jumps from an orbit of energy E_1 to one of energy E_2 is equal to $(E_1 - E_2)/h$. Since the wave number is equal to ν/c, where c is the velocity of light, the wave number associated with a transition from an orbit of quantum number n_1 to one of quantum number n_2 will be :

$$\frac{2\pi^2me^4}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad . \quad . \quad . \quad . \quad \text{I} \quad (7)$$

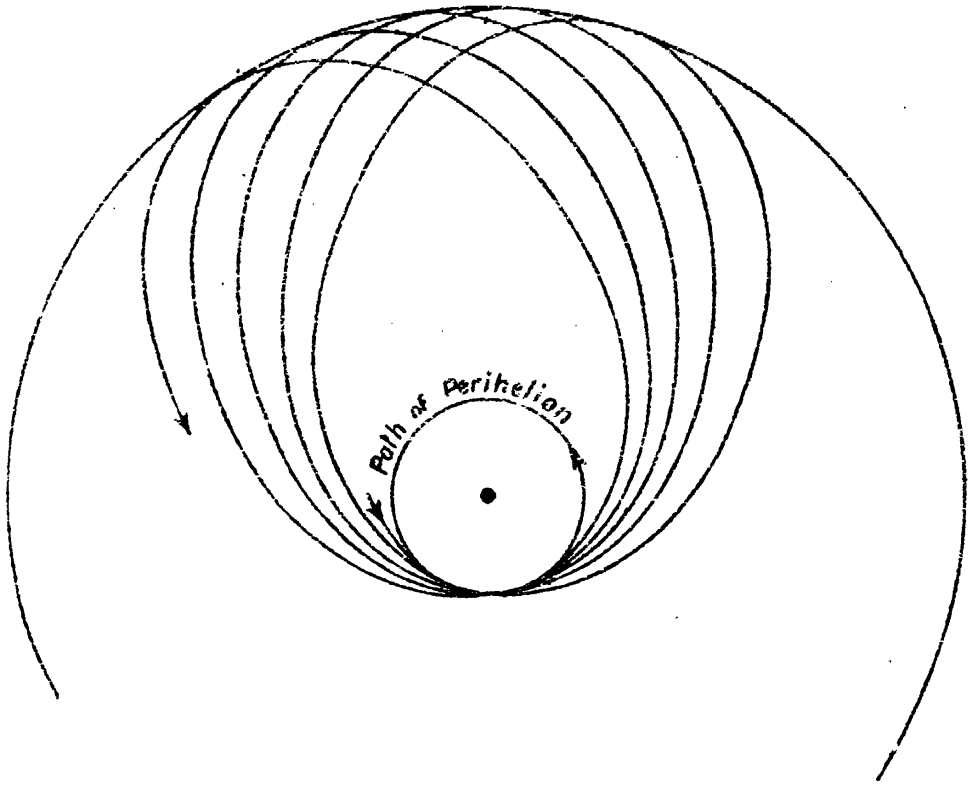
where $$R = \frac{2\pi^2me^4}{ch^3}$$

This agrees with the fact that some of the lines of the hydrogen spectrum can be classified in series whose wave numbers involve the differences of the reciprocals of the squares of whole numbers. The arbitrary assumptions of the theory were, of course, chosen to explain this fact, and the really striking point about the theory is not so much that it predicts the above types of series, as that the numerical value of the *Rydberg Constant, R*, is almost exactly that required by experiment, and an exact agreement is obtained when the theory is elaborated so that the electron is regarded as revolving not with the nucleus as the centre of revolution, but about the centre of gravity of the nucleus and the electron together, this being, of course, the more correct assumption.

The circular orbit is the simplest example of the more general type of orbital motion, which is that of an ellipse with the nucleus at its focus. The Bohr theory was extended to the case of elliptical orbits with the additional complication of the variation of the mass of the electron, in accordance with the Theory of Relativity.* In the original theory of elliptical orbits, each electron state is characterized by two quantum numbers n and k. The principal quantum number, n, is a measure of the total energy of the orbit, the negative energy varying inversely as n^2 in hydrogen-like atoms, whilst the major axis of the ellipse is also proportional to n^2, so that the orbits become larger with increasing n. The secondary quantum number, k, is a measure of the angular momentum of the orbit, which is equal to $kh/2\pi$. The ratio k/n gives the ratio of the minor to the major axis of the ellipse, and

* According to the Theory of Relativity, the energy of a material particle at rest is equal to m_0c^2, where m_0 is the rest mass of the particle and c the velocity of light. The mass, m, of a particle moving with velocity u, is given by the relation $m = m_0 \Big/ \sqrt{1 - \frac{u^2}{c^2}}$, so that the mass varies with the velocity, but the effect is only appreciable at very high velocities. The total energy of a particle moving with velocity u is equal to $mc^2 + V$, where V is the potential energy, and if u is small compared with c, the total energy is equal to $m_0c^2 + \frac{1}{2}m_0u^2 + V$. Here m_0c^2 is called the mass energy of the particle, and $\frac{1}{2}m_0u^2$ is the kinetic energy.

thus determines its eccentricity; k can have any value from 1 to n, and in any one hydrogen-like atom all orbits with a given value of n have the same major axis of the ellipse. The orbit for which $k = 1$ is the most eccentric of those with a given value of n, and is hence the orbit in which the electron travels farthest from the nucleus, whilst the orbits for which $n = k$ are circular. In the elliptical orbits, the velocity and hence the mass of the electron vary with its distance from the nucleus, and the effect of this is to produce a precession of the orbit as shown in Fig. 2. This precession is very slow compared with the time of a complete revolution in any one orbit, and in



[*Courtesy G. Bell and Son.*

FIG. 2.—To illustrate the precession of an elliptical orbit.

the orbits for which the effect is greatest, the electron travels round the ellipse about 40,000 times for each revolution of the major axis. This refinement of the theory was due to Sommerfeld, and it led to a fairly satisfactory theory of the hydrogen atom, although it was necessary to introduce a third quantum number in order to explain some of the facts. The theory also led to an explanation of the spectra of the positive ions He^+ and Li^{++}, which consist of one electron revolving round nuclei of charge $+ 2e$ and $+ 3e$, respectively. Some progress was also made in the interpretation of the spectra of more complex atoms, particularly those, such as the alkalis, whose spectra showed resemblances to that of hydrogen. The alkali metals are univalent and their free

atoms contain one relatively loosely bound electron (see p. 60), which was regarded as revolving round the " core " formed by the nucleus and the inner electrons. A distinction was made between " non-penetrating " orbits, in which the electron remained outside the core during the whole of its trajectory, and " penetrating orbits " in which the electron, when nearest to the nucleus, plunged into the region in which the electrons of the core were moving. In this region the attraction of the nucleus was no longer of the inverse square type, and the effect of this was to give a motion analogous to that of Fig. 2, but with a much more rapid revolution of the axis of the ellipse, so that there were only a few branches of the rosette to each complete revolution of the major axis of the ellipse.

In spite of its great success, the Bohr theory was not completely satisfactory, for in the first place facts were found with which it did not agree, and, secondly, it involved a logical inconsistency, in that when an electron was moving in an orbit, it was assumed to obey the laws of classical mechanics, though these were subjected to the apparently quite arbitrary restrictions of the quantum hypothesis. The solution to this difficulty was found, not by making further arbitrary assumptions, but by recasting the laws of mechanics into a new mathematical framework, and we may approach this difficult subject by considering first some points in connection with the Uncertainty Principle of Heisenberg.

SUGGESTIONS FOR FURTHER READING.

For a detailed account of the Bohr theory, the reader may consult:

Andrade, E. N. da C. " The Structure of the Atom." London: 1927 (G. Bell and Son).

Sidgwick, N. V. " The Electronic Theory of Valency." Oxford: 1927 (Clarendon Press).

Chapter IV.—The Uncertainty Principle of Heisenberg.

If the previous pages are examined critically, it will be seen that they involve the assumption that quantities such as position, velocity, momentum, &c., may be ascribed to an electron at any instant, and that these quantities have the physical meanings associated with them in the classical mechanics. From the modern viewpoint, it is meaningless to speak of a physical quantity unless we can describe a method which, if not yet actually realizable, will at least in principle enable us to measure the quantity concerned. If we consider the ordinary methods of measuring quantities such as position, velocity, &c., it will be seen that they all involve the assumption that we can ignore most of the alteration produced by the act of measurement. If, for example, we measure the length of a body, we must compare it with a standard scale. If this is done by making contact between one body and another, we are uncertain as to the exact deformation produced by the actual contact. If we seek to overcome this difficulty by using a beam of light to compare the object with the scale, the indicating beam of light exerts a pressure, and we are again uncertain as to the exact deformation caused. With ordinary objects these effects are so small as to be negligible, but when we come to consider electrons, the position is very different.

The usual illustration of the Heisenberg Principle is that of an attempt to measure the simultaneous position and velocity of an electron. To do this we might in principle * use two microscopes and a beam of light, and so observe the positions of the electron at two instants of time and hence deduce its velocity. The resolving power of a microscope is limited, and is given by the relation $\Delta x = \frac{\lambda}{\sin\theta}$, where λ is the wave-length of the light employed, and 2θ the aperture of the objective. The accurate measurement of position therefore involves the use of light of a very short wave-length and of an objective of high aperture, the objective receiving light from all directions included within the angle 2θ. The work of Compton has, however, shown that when light interacts with an electron, the latter undergoes a recoil, the process being known as the *Compton Effect*. This process is a typical quantum phenomenon in which a ray of light of frequency ν behaves as though it consisted of a stream of particles or *photons* each of energy

* The experiment is a purely hypothetical one.

$h\nu$, where h is Planck's constant. The observation of the electron requires interaction with at least one photon, and in this case if we imagine the photon to travel along the x-axis and to be scattered through an angle α, the electron acquires a momentum whose component in the x direction is $\frac{h\nu}{c}(1 - \cos\alpha)$, where c is the velocity of light. The observation of the first position of the electron will therefore alter the velocity of the electron by an amount which increases with ν (*i.e.*, as the wave-length becomes smaller) and which cannot be estimated exactly, because the objective of high aperture receives light from the whole range of the angle 2θ. We see, therefore, that the very factors which favour the accurate measurement of the position produce the greatest uncertainty in the velocity and *vice versa*. No method can be devised which avoids this difficulty, and the Uncertainty Principle of Heisenberg states that if Δx is the uncertainty in the position and Δp the uncertainty in the momentum, then the product $\Delta x \Delta p$ has a minimum value of h, where h is Planck's Constant of Action.

This principle is not confined to the above case. If, for example, we try to measure the energy, E, of a particle at a particular instant of time, t, we find that the conditions necessary to produce the greatest accuracy for the energy are those which produce the greatest uncertainty in the time, and again $\Delta E \Delta t \not< h$. This implies that if we are dealing with an electron in a stationary state the latter will only have an exact energy if the time is completely indeterminate. If we deal with a restricted period of time, then there will be a slight uncertainty in the energy. With periods of time of the order of one second, the effect is negligible, because of the small value of the constant h, and it is for this reason that we usually obtain sharp spectral lines, whose frequencies are connected by the relation

$$E_1 - E_2 = h\nu$$

In some cases an atom may go through a series of changes, in which it passes through a number of energy states $E_1, E_2, E_3 \ldots$ In such a case it may happen that one of the states has a very brief existence, and if so its energy is slightly uncertain, in accordance with the Heisenberg Principle, and a diffuse spectral line results.* This effect has, in fact, to be considered in the study of the soft X-ray spectra of solids, which has thrown great light on the nature of metals. Similarly, if we try to measure the angular momentum, M, of a particle revolving round a fixed point, and the angle ω made with some fixed reference line by the line joining the particle to the fixed point, the uncertainties are given by

* There are, of course, many other factors which may produce diffuse spectral lines.

$\Delta M \Delta\omega \not< h$. It will be noted that in all the above cases, the product of the two quantities connected by the Uncertainty Principle has the dimensions * ML^2T^{-1}, *i.e.*, the dimensions of *action* (see p. 27). It will be noted that the Principle refers to the product of the two uncertainties and refers only to the minimum value of this product.

In considering the meaning of the Uncertainty Principle we may adopt two points of view. On the one hand, we may argue that our methods of measurement are at fault, and that if these could be perfected we could measure the real momentum and position at the same time. This clearly leads to difficulties about the meaning of reality, since we are practically compelled to say that by the "real position and momentum of an electron at a given instant" we mean something which, by the very nature of things, we cannot measure. Apart from this we should still be left with the problem of how the electron would behave in the hypothetical world where momentum and position, energy and time, &c., could be measured simultaneously. Without going into details, it may be said that this line of approach has failed.

The alternative is to accept the Uncertainty Principle as embodying a real characteristic of the physical world, which had escaped our notice in large-scale phenomena, because the magnitudes involved are very much larger than Planck's constant h, but which is of supreme importance in connection with the behaviour of particles of such small mass as an electron. It is from this point of view that such great progress has been made, though examination will show that a very strange world is being visualized. Suppose, for example, that we consider an electron contained in a one-dimensional box of length L. Then the Uncertainty Principle implies that the particle cannot be at rest, for if it were at rest its velocity would be exactly zero, and if this were so the uncertainty in its position would be infinite, and it would not be confined to the length L. Even at the absolute zero of temperature, we are thus led to expect some motion, although the effect is only appreciable when the length L is of atomic dimensions. Heisenberg's Principle then states that the uncertainty in momentum must be at least h/L, and we cannot consider changes of momentum of less than this, since to do so would imply that the uncertainty in momentum was less than h/L, and the electron would therefore not be confined to the length L. These considerations clearly lead to great difficulties if we try to describe small-scale events in terms of our usual ideas of space and time, since we have become so accustomed to imagining that each of the

* Position has dimensions L, and mass M, and velocity L/T, so momentum multiplied by position has dimensions ML^2T^{-1}. The technical expression is that two quantities which are canonically conjugate cannot be measured exactly at the same instant.

properties, position, velocity, kinetic energy, momentum, time, &c., can be defined exactly, without reference to the others, that we find it difficult to form a mental image of the restrictions imposed by the Uncertainty Principle. In the methods developed by Heisenberg and Dirac, all attempts to describe phenomena in terms of our usual concepts of space and time are given up, and are replaced by systems of mathematics, which deal only with the quantities we actually observe, and express these in suitable mathematical forms. Although quantitatively satisfactory, these methods are difficult to visualize, and for the non-mathematician it is more easy to consider the alternative line of approach, the so-called *wave mechanics* of Schrödinger, since this expresses some of the results in a way to which we are already accustomed. The methods of Dirac, Heisenberg, and Schrödinger are mathematically equivalent, as of course they must be if each is to lead to the correct answer, but some of the results of wave mechanics can be visualized, although care is necessary to avoid using the wave analogy unjustifiably.

Note: It has been pointed out that confusion may arise from the fact that different authors formulate the Uncertainty Principle in different ways. The reason for this is discussed on p. 284.

Chapter V.—The Ideas of Wave Mechanics.

In the preceding sections we have described the general failure of ordinary mechanics to deal with problems of atomic structure, and we have seen how Heisenberg's Principle suggests that when we consider events on the atomic and electronic scale we can no longer regard properties such as position, time, velocity, momentum, kinetic energy, &c., as being defined exactly and independently without reference to one another. If we ignore the historical development of the subject and consider the experimental evidence alone, we may say that the solution to these difficulties lies in the fact that electrons have been shown to give rise to diffraction and interference effects. This discovery was made first by Davisson and Germer (1927), and by G. P. Thomson (1927), who showed that diffraction patterns could be observed and recorded photographically when beams of electrons were reflected from crystals. This remarkable discovery showed that electrons possessed the properties of waves as well as of particles, and a beam of electrons of velocity u was found to behave as though it were associated with waves, of wave-length λ, given by the relation

$$\lambda = \frac{h}{p},$$

where h is Planck's constant, and p = momentum.

For electrons whose velocity is much smaller than the velocity of light, c, the momentum p may be put equal to mu, and the relation reduces to:

$$\lambda = \frac{h}{mu}.$$

For abbreviation we shall always use this simplified form, and this relation is the basis of the methods of investigating crystal structure by electron-diffraction technique; considered experimentally it is the foundation of the whole of the modern theory of atomic structure and of the properties of metals.

We see, therefore, that the electron which was at first thought to possess only the properties of a charged particle, exhibits also characteristics which are usually associated with waves, and it is well known that light shows a similar dual character. In this respect the development of optical theory may be divided into three well-marked stages. The older science of *Geometrical Optics* dealt with the passage of rays of light from one point to another, and led to the dis-

covery of the laws of reflection and refraction. The fact that light rays travel in straight lines in a uniform medium naturally suggested that light consisted of streams of particles or corpuscles, and a corpuscular theory of light was advanced by Sir Isaac Newton. The discovery of interference phenomena led to the development of the wave theory of light by Huygens (1690) and others. This theory accounted satisfactorily for the large-scale phenomena of geometrical optics, and provided such a beautiful explanation of so many additional effects (interference, dispersion, &c.) that by the end of the nineteenth century, the corpuscular theory of light was almost completely discarded, and the wave theory was universally accepted and was often thought to imply that light consisted of waves in a definite medium, the so-called *ether*.

The wave theory, however, led to great difficulties when the quantum phenomena were discovered. In this class of phenomenon—the photoelectric effect and the Compton effect are examples—the evidence seemed overwhelming that light of frequency ν gave up its energy in definite quanta equal to $h\nu$, where h is Planck's constant. This behaviour seemed impossible to reconcile with any picture in which the energy was associated with the whole of an expanding wave-surface, and clearly suggested the existence of light particles or *photons* with kinetic energy $h\nu$. There was thus an apparent conflict between the wave and particle properties of light, and the position was made more confused by the fact that all experimental attempts to detect the hypothetical " ether " resulted in complete failure.

This conflict between the two theories of light was solved by a compromise which may be summarized briefly as follows :

(1) A light ray is to be regarded as a stream of moving particles or photons, light of frequency ν being composed of photons of kinetic energy $h\nu$. In this sense the old corpuscular theory is correct, and whenever we observe light we observe one or more whole photons.

(2) When we wish to calculate the intensity of light, *i.e.*, the density of photons or the probability of finding a photon at a particular place, we use the equations of the wave theory with the assumption that the square of the amplitude of the waves is proportional to the light intensity. In an interference experiment, for example, the dark areas of low intensity are the regions where the wave equations indicate a small amplitude, and this is to be interpreted as a *small probability* of finding a photon at the place concerned.

In this way the whole of the mathematical framework of the wave theory is retained, but we no longer imagine the existence of a vibrating medium. Light does not involve any actual physical vibration,

and although as a matter of convenience we still speak of light waves, wave-lengths, frequencies, &c., what we really mean is that the intensities of light can be calculated by wave equations, with the interpretation that the square of the amplitude is proportional to the probability of finding a photon at the place concerned.

(3) The interpretation of the wave theory in terms of probabilities applies not only to beams of light consisting of streams of photons, but also to the behaviour of an individual photon, and this implies that there is some degree of uncertainty in the behaviour of the individual photon. If, for example, we pass rays of light through a diffraction apparatus, we may obtain on a screen a series of bright and dark rings, the former being at the places where the amplitude of the wave equation is large and the latter where it is small. If now we pass one single photon through the same apparatus, we cannot predict where the photon will travel. All that we can say is that there are different probabilities of its travelling in different directions, these probabilities being greatest in the directions corresponding to the light rings observed when a stream of photons is passed through the apparatus. There is thus a certain indeterminancy in the behaviour of the individual photon, analogous to the behaviour of the electron according to Heisenberg's Principle. If, for example, we pass light through an aperture, then the smaller the aperture the greater is the diffraction effect, so that the more the aperture restricts the cross-section of the beam the greater is the uncertainty of the direction of the individual photon after passing through the aperture. Effects such as these can readily be described in terms of probabilities, but it is, of course, quite impossible to describe them in terms of either the older geometrical optics or in terms of the simple particles of the early corpuscular theory. The use of wave equations with a probability interpretation does not enable us to "understand what is happening," but it places us in a position in which we can describe and predict experimental results in terms of the appropriate probabilities, and can include both the wave and particle aspects of light in one theory. It will be noticed that this increased power is gained at the cost of an admission that we cannot always follow the individual photon in detail along its path. In the experiment referred to above, for example, nothing enables us to predict which direction the individual photon will take after passing through the diffraction apparatus. We may calculate exactly the relative probabilities of the photon moving in different directions after passing through the apparatus, but we then reach the limit of our powers, and the rest is indeterminate and unpredictable.

We have seen that electrons give rise to diffraction effects as though

they were associated with waves, and it is therefore natural to enquire whether the wave-like and the particle aspects of an electron can be united in one single theory, as has been done for the case of a photon. Clearly, so far as the simple diffraction effects are concerned, the problem can be approached in the same way, and we may develop a "probability wave theory" of electrons on the assumption that the electron is a particle, and that the amplitude of a wave equation is a measure of the probability of finding an electron at the place concerned. The question then arises as to whether the wave-like characteristics of electrons may affect their behaviour in other ways, and here an examination of the relation $\lambda = \frac{h}{mu}$ is instructive.

We know from experiment that an electron is accelerated or retarded by an electric field, with a corresponding change in its momentum, mu. From the relation $\lambda = \frac{h}{mu}$ it follows that the wave-length associated with the electron is inversely proportional to its momentum, and we can see, therefore, that as the electron accelerates, the wave-length will change. We have, thus, a condition of affairs in which as an electron moves through a field of varying potential, the associated wave-length is continually changing. Speaking generally, it may be said that if the changes in potential are appreciable only over distances which are large compared with the associated wave-length, the electron moves more or less as though it were a "particle" obeying the laws of "ordinary mechanics." If, however, the changes in potential are appreciable over distances of the order of a wave-length, some completely new phenomena are met with, and these cannot be explained in terms of the older mechanics. In the following pages we shall describe the general methods by which mechanics has been re-moulded so as to take into account these wave-like characteristics of the electron, this branch of mechanics being known as "Wave Mechanics." General considerations of the magnitudes involved in the relation $\lambda = \frac{h}{mu}$ show that the wave-lengths associated with electrons in atoms are of the same order as the "sizes" of the atoms, or of the distances between atoms in metallic crystals. Under these conditions the wave-like characteristics of the electrons produce many strange effects, and some of these are directly responsible for the properties of metals. Many of these effects can be understood only in terms of the new mechanics, and if the metallurgist wishes to understand the behaviour of electrons in metals, it is essential for him to understand the ideas which underlie wave mechanics. In the following pages we shall describe the main steps

or lines of argument by means of which the mathematicians passed from the old to the new mechanics, but we shall present the results dogmatically and not concern ourselves with mathematical technique. We have adopted a rather formal method of approach, not merely because of its historical and logical interest, but because it serves to emphasize the correct way of regarding the wave-like characteristics of electrons. The reader who does not wish to follow the argument may note that the method adopted is to re-write the laws of mechanics in a form which is mathematically similar to certain equations of optical theory. In this way a problem of the motion of a beam of electrons in a varying field of force is made mathematically similar to a problem of the passage of a ray of light in a medium of varying refractive index. This involves the setting up of a differential wave equation, the interpretation of which is discussed in Chapter VI.

In the preceding chapters we have referred to the circular orbits of classical mechanics. These are merely one particular example of the more general problem of the motion of a particle in a variable field of force, and we shall assume that the reader is familiar with the elementary equations of dynamics by means of which we can calculate the motion of a particle under different conditions of attraction, repulsion, &c. These different equations may be expressed in more generalized forms, one of which is the *Principle of Least Action* of Maupertuis (1698–1759), and this may be understood in the following way. We may suppose that we wish to shoot a particle of given total energy E from a point A to a point B (Fig. 3), subject to the condition that potential energy, W, and kinetic energy, K, may be interchanged, but that the total energy $E = W + K$, remains constant. Then clearly the path which the particle will follow depends on the field of force in the space between A and B. In the absence of a field, the particle will travel in a straight line from A to B. In the presence of a uniform field such as the gravitational field of the earth, we should have to " aim " the particle upwards from A, and the path followed would be a parabola. The Principle of Least Action then states that if for all conceivable paths from A to B, we evaluate the integral $\int_A^B 2K dt$, where t is the time, then this integral will have a minimum value * for the actual

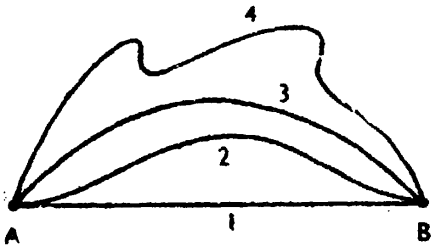


FIG. 3.

* Strictly speaking we should refer to a stationary value rather than a minimum value, but for a simplified description, the latter may be accepted.

mechanical path. That is to say that, if in Fig. 3 we evaluated the above integral for a series of different paths 1, 2, 3, 4 . . ., then in the absence of a field of force, the minimum value of the integral would be obtained for the straight-line path No. 1, whilst the correct parabola would be predicted for the gravitational problem, and similarly with more complicated fields. For simple problems this principle has no advantage over the usual equations of motion, but for complicated problems it is sometimes more convenient. The integral $\int_A^B 2K dt$ defines the quantity known as "action," and this has the dimensions of ML^2T^{-1}. It will be noted also that the value of the integral depends only on the space co-ordinates of A and B, and not on the time. The minimum value of this integral for the actual mechanical path may be called S.

The above remarks refer to the trajectory of a particle on passing from one point to another, and we may now consider the analogous problem of the passage of a beam of light from one point A to another B. In this case we know that the path of the beam of light depends on the refractive index, and hence on the velocity * of light in the space between the two paths. If the refractive index is uniform, light travels in a straight line from A to B, just as in the mechanical problem the particle travelled in a straight line from A to B in the absence of a field of force. If the refractive index is not uniform between A and B, the light travels in a path which is bent or curved, and which depends on the exact variation of the refractive index. The science of Geometrical Optics deals with this kind of problem, and the well-known laws of reflection and refraction enable us to deduce the path of a beam of light when the variation of refractive index and the positions of reflecting surfaces are known in the space surrounding A and B. Just as the Laws of Mechanics could be generalized in the form of the Principle of Least Action, so the Laws of Geometrical Optics may be generalized in a form known as *Fermat's Principle of Least Time*. This states that if in a problem where the variation of refractive index is known we consider a large number of conceivable optical paths for a beam of light travelling from A to B, then the actual optical path which the light follows is characterized by a minimum † value of the integral:

$$\int_A^B \frac{ds}{v},$$

where v is the velocity of light at the place ds, and ds is an element of

* The velocities of light in different media are inversely proportional to the refractive indices of the different media.

† See footnote to p. 26.

length of the path. This implies that of all conceivable paths the light travels by the path which enables it to reach B as quickly as possible, and this principle enables the laws of reflection and refraction to be predicted.

It will be seen, therefore, that there is a certain resemblance between the laws governing the trajectories of particles in the mechanical problem and the paths of beams of light in the optical problem, since in each case the actual path followed is characterized by the minimum value of an integral. Further, in a general way it can be seen that the variation of the refractive index in the optical problem plays the same part as the field of force or potential in the mechanical problem. This correspondence can be expressed in a precise mathematical form, so that the problem of the motion of a particle in a field of force becomes mathematically similar to the problem of the path of a ray of light in a medium of variable refractive index. These resemblances between the equations of mechanics and geometrical optics were noted many years ago by Hamilton, and were long thought to be nothing more than an interesting mathematical coincidence; it was only with the work of de Broglie and Schrödinger that it was realized that a supremely important principle lay concealed.

So far we have described the correspondence between the mechanical problem of the trajectory of a particle in a field of force and the optical problem of the path of a ray of light in a medium of varying refractive index, and we have discussed this in terms of the older geometrical optics. It is well known that the laws of geometrical optics can be expressed in terms of the wave theory of light, and all the equations for the paths of rays under conditions of reflection, refraction, &c., can be expressed in terms of the wave theory. For simple problems of geometrical optics, no advantage is gained by using the wave theory, but when we deal with problems in which the refractive index varies appreciably over distances of the order of one wave-length, the wave theory predicts a large number of new effects (dispersion, diffraction, &c.) which were quite inexplicable in terms of the older theory of rays. We see, therefore, that the change from the older geometrical optics to the wave theory did not affect what may be called large-scale phenomena (paths of rays, reflection, &c.), but accounted for a number of small-scale phenomena which could not otherwise be understood. Since the change from geometrical optics to wave theory does not affect the large-scale phenomena, the correspondence between the equations of mechanics and those of geometrical optics to which we have referred above can be expressed as a correspondence between the equations of mechanics and those of the wave theory of light. In this

way it is possible to rewrite the equations of mechanics in forms which are mathematically similar to those of a wave theory. If this is done, the new equations naturally contain terms which play the same part that wave-lengths, frequencies, &c., would play if the equations actually referred to a wave motion. The mathematical correspondence is so complete that for many purposes it is justifiable and helpful to visualize the equations as though they were equations of a wave motion. In this way we may think of a moving particle as being associated with wave-lengths, frequencies, &c., but we must remember that this is only a convenient way of visualizing the equations, and does not imply the existence of any physical waves.

As stated above, it is possible to rewrite the equations of mechanics in forms which are mathematically similar to those of a wave theory. So long as we are dealing with large-scale problems, this procedure has no advantage, and it was at first looked upon as being little more than clever mathematical jugglery. The genius of de Broglie and Schrödinger lay in the fact that they were prepared to carry out the transformation of the equations of mechanics to those of a wave theory, and at the same time to hold fast to the correspondence between the effect of a field of force in the mechanical problem and of a varying refractive index in the optical problem, and to carry this correspondence to its logical conclusion. In the optical problem a variation of refractive index which is appreciable over the distance of a wave-length produces effects which cannot be explained in terms of the older theory of rays. Hence it was suggested that in the mechanical problem a variation of force over very small distances might produce effects which could not be explained in terms of the older mechanics. But these effects might be expressed in terms of the new equations, because these transformed equations were those of a wave theory, and a wave theory was able to deal with the effects observed when the refractive index varied appreciably over a distance of the order of a wave-length. In this way by rewriting the equations of mechanics in a form similar to that of a wave theory, and by retaining the correspondence between force and variation of refractive index, it was possible to build up a new mechanics, the so-called "wave mechanics," which predicted new effects when the force varied greatly over very small distances and was thus directly applicable to the problem of the motion of an electron in the field of an atom or in the periodic field of a crystal lattice. It need scarcely be said that in its early stages this development of mechanics was regarded as little but mathematical speculation, but the whole position was transformed when it was discovered that electrons showed diffraction effects as though they were somehow associated with waves.

This discovery showed that the rewriting of the laws of mechanics in the form of equations of a wave theory was not just an example of mathematical ingenuity, but had revealed a real characteristic of the physical world. It is highly important for the student to realize that wave mechanics arose before the discovery of the wave-like properties of electrons, and as the result of pure mathematical reasoning which showed how the equations of mechanics could be rewritten in the form of a wave theory.

The student who wishes for further details will find these in the Appendix on p. 32. For the general reader it is sufficient to note that wave mechanics came into being as the result of the line of argument described above. When the equations of mechanics are transformed into those of a wave theory, there are naturally relations between the terms of the wave equations and the dynamical properties such as momentum, energy, &c. In our comparison of the optical and mechanical problems we have dealt with the similarity between the laws governing the paths of particles and of rays of light, and have not considered the individual photons. Our first description should therefore refer to beams of electrons, rather than to single electrons or other particles.

Historically it was first pointed out by de Broglie that if waves were associated with particles, then the Principle of Relativity indicated that:

$$\frac{\text{Energy}}{\text{Frequency}} = \frac{\text{Momentum}}{\text{Wave number}} = \text{Constant} \quad . \quad \text{I } (9a)\ (9b)$$

The constant was then intuitively identified with Planck's constant, h, and since the above relations were known to hold in the case of light (energy $h\nu$, momentum $h\nu/c$) it was suggested that they might also apply to particles. The second of these relations was then confirmed experimentally by the electron-diffraction experiments of G. P. Thomson and of Davisson and Germer, which showed that electrons of velocity u were diffracted by a crystal as though they possessed a wave-length equal to $\frac{h}{mu}$.* Considered experimentally, this relation between wave-length and momentum is the foundation of the whole subject. It could therefore be concluded that the first of the above relations would also be satisfied, and the arguments of de Broglie showed that for particles, $h\nu$ would be equal to the relativity energy E_m given by:

* As explained on p. 22, this relation requires modifications if the velocity u is very great.

$$E_m = \frac{mc^2}{\sqrt{1 - \frac{u^2}{c^2}}} + W \quad . \quad . \quad . \quad . \quad \text{I (10)}$$

which for ordinary problems where the velocities are small compared with that of light is the same as :

$$h\nu = E_m \simeq mc^2 + \tfrac{1}{2}mu^2 + W \quad . \quad . \quad \text{I (11)}$$

The energy E_m thus includes the energy mc^2 associated with the mass of the particle. It may be thought curious that we should suddenly change from the ordinary total energy $E = \frac{1}{2}mu^2 + W$, to the total energy E_m, but it must be remembered that the potential energy, W, has always to be measured from some arbitrary zero, so that the addition of the constant term mc^2 is merely equivalent to a shift in the zero from which the potential energy is measured, and consequently it does not affect the problems which we have been discussing. As will be appreciated from what follows the absolute value of ν is never required,* and the physical properties dealt with involve either the differences between two frequencies or the differential of the frequency, for which the constant term mc^2 is not involved.† We have, therefore, the two fundamental relations :

$$E_m = h\nu \quad . \quad . \quad . \quad . \quad . \quad \text{I (12}a\text{)}$$

$$\lambda = \frac{h}{mu} \quad . \quad . \quad . \quad . \quad . \quad \text{I (12}b\text{)}$$

In the wave mechanics developed by Schrödinger, the essential assumption made was that the waves were of a sine form, and it could then be shown that the above two relations (12*a*) and (12*b*) were those necessary to make the mathematics self-consistent. That is to say, it could be shown that if the hypothetical waves were of a sine form, in the equations of which the time t entered as a term $2\pi\nu t$, then the mathematical scheme became consistent if the frequency ν were directly proportional to the energy.‡ In some books the reader will find the relation (12*a*) deduced in this way as the relation necessary to produce a consistent scheme, and in the same way the relation (12*b*), which has a direct experimental basis, fits into the general scheme.

* Thus N. F. Mott ("An Outline of Wave Mechanics") writes $\nu = E/h$, and for the problems with which he is concerned the change makes no difference although the frequencies are enormously smaller than those given by $\nu = E_m/h$. This may serve to emphasize the purely symbolic and mathematical nature of the hypothetical waves.

† The reader should be warned that in some books the same symbol is used indiscriminately for E and E_m, and much confusion is caused in this way.

‡ The general equation of a sine wave is of the form $\sin 2\pi(\nu t - x/\lambda + a)$.

We have, therefore, now carried our discussion to a point at which the mechanical problem has reached the second stage of the optical theory (p. 23), because the hypothetical waves have been associated with frequencies and wave-lengths which agree with the observed interference phenomena.

From the above relations it will be seen that the velocity of the hypothetical waves is given by :

$$U = \nu\lambda = \frac{E_m}{mu} \simeq \frac{mc^2 + \frac{1}{2}mu^2 + W}{mu} \quad . \quad . \quad \text{I (13)}$$

In most ordinary problems, the term mc^2 is so much the greatest that U is of the order c^2/u, and since u can never be greater than c, this implies that U must always be greater than c. This serves to emphasize * that the waves are merely mathematical functions, and are not of any material nature, because nothing material can travel faster than light. The velocity U is called the phase-velocity of the waves, and gives the velocity with which the waves travel. U is thus greater than c, and consequently U cannot be the velocity of the actual electron, since this cannot exceed c. We shall consider later what function gives the velocity of the electron itself, and for the present we may say that the argument leads to the conclusion that moving electrons can be treated mathematically as though they were associated with waves of phase-velocity c^2/u, where u is the velocity of the electron.

We have seen how the laws which express the motion of streams of electrons can be manipulated mathematically into a form which resembles that of the optical theory, and we have now to see how the electron density, *i.e.*, probability of finding an electron at a particular place, is to be calculated, and, as in the case of the optical theory, the interpretation is that the amplitude of the hypothetical waves is a measure of the electron density at the place concerned.

Appendix to Chapter V.

We have described above how the Principle of Least Action enables the trajectory of a particle to be predicted as the path which gives a minimum value to the integral $\int_A^B 2K dt$. For convenience we may denote the minimum value of this integral for the actual mechanical path by the symbol S. We have also explained how in the optical problem the Principle of Least Time enables the path of the ray

* We have reproduced above the description which the reader will usually find in the text-books. A little consideration will show that since the potential energy W has to be measured from some arbitrary zero, the frequency ν cannot be uniquely defined, because W in equation I (11) may have any arbitrary constant added to it. On the other hand, the difference between two frequencies and the differential of the frequency do not involve the constant term.

of light to be predicted as that which gives a minimum value to the integral $\int_A^B \frac{ds}{v}$. The laws of geometrical optics can be expressed in terms of the wave theory, and the Principle of Least Time can be interpreted in terms of this theory. For this purpose we may again consider the passage of a beam of light from A to B, and we may denote the minimum value of $\int_A^B \frac{ds}{v}$, which characterizes the actual optical path, by some symbol, say Y. The value of Y is determined by the space co-ordinates of A and B, so that if the light starts from A and travels to B, the value of Y at the point B, say Y_B, can be calculated if the variation of the refractive index in the surrounding space is known. Clearly there are many other points surrounding A, such that if light travelled from A to the points concerned the value of Y would also be Y_B, and we can imagine A surrounded by a surface characterized by the fact that if light travelled from A to any point on the surface, the value of Y would be Y_B. If the surrounding space were homogeneous, this surface would be a sphere, whilst if the refractive index were a variable the shape of the Y surface would change accordingly. Since $\int_A^B \frac{ds}{v} = \int_A^B dt$, where t is the time, this surface will represent the ends of all possible rays of light leaving A at the time $t = t_0$, and travelling for the same time that the one ray of light took to travel from A to B. In this way we can imagine the space round A to contain a number of surfaces Y_1, Y_2, Y_3 . . . corresponding to the positions at times $t = t_1$, t_2, t_3, &c., of the ends of all possible rays of light leaving A at the time $t = t_0$. In the wave theory, the wave front is then regarded as an expanding surface which spreads out from A parallel to the Y surfaces, and the rays of light are perpendicular to the wave surface.

In the mechanical problem we have denoted by S the minimum value of the integral $\int_A^B 2K dt$ which characterizes the actual mechanical path of the particle from A to B. It is clear, therefore, that S in the mechanical problem corresponds with what we have called Y in the optical problem. Just as in the optical problem we regarded A as surrounded by surfaces of constant Y, so in the mechanical problem we may regard A as surrounded by surfaces of constant S, the meaning of these being that if the particle travels from A to any point on the surface concerned, say S_n, the value of the integral $\int_A^{S_n} 2K dt$ is the same. We have now to enquire whether a mathematical function can be found which may be interpreted as an expanding surface spreading out parallel to the S surfaces, in the same way that the wave surface spreads out parallel to the Y surfaces in the optical problem. The function chosen is called the *action function*, and is often denoted S^*. If we confine ourselves to cases where the energy, E, remains constant, S^* is given by:

$$S^* = S - E(t - t_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{I (14)}$$

where t is the time considered and t_0 is the time at which the particle leaves A. In this way the Principle of Least Action is combined with a mathematical function which may be interpreted as an expanding surface, and a further analogy with the optical theory has been obtained.

The way in which equation I (14) represents an expanding surface may be shown by considering a simple case where $t_0 = 0$ and $E = 1$, so that $S^* = S - t$. Suppose we consider the S surfaces surrounding A, for which $S = 100$, 101, 102 . . . then at time $t = 0$, the surface $S = 100$ corresponds with $S^* = 100$. At time $t = 1$, $S^* = 100 - 1 = 99$, and it is the surface $S = 101$ which now corresponds with the surface $S^* = 100$. Consequently, the surface $S^* = 100$ has moved outward, and similarly with further increase in the time. It is not possible to give any simple physical interpretation of the action function, and historically it was introduced as a piece of mathematical jugglery, which was only shown later to be of practical significance. The action function must therefore be looked on as a mathematical function associated with a moving particle.

It can also be shown that the momentum of the moving particle is perpendicular to the S^* surface, just as the direction of the ray of light was perpendicular to the wave surface in the optical problem.

In the study of light, the wave theory and the older geometrical optics lead to the same results for large-scale phenomena, and the "wave" aspect of light only becomes apparent when we are concerned with distances of the same order as that of the wave-length. In the above discussion we have shown that the Principle of Least Action in the mechanical problem can be reconciled with the concept of the spreading surface of the action function S^*. The bold concept of wave mechanics was then that this surface of the action function S^* could be united with equations analogous to those of the wave theory of light, so that the S^* surface could be regarded as associated with waves, although, just as in the optical problem, these waves are not waves in any physical medium, but are to be interpreted on a probability basis. As explained on p. 31, the essential assumption made by Schrödinger was that the hypothetical waves associated with the expanding S^* surface were of a sine form, and it could then be shown that the mathematics became consistent if the fundamental relations of equations I (12*a*) and I (12*b*) were satisfied. The reader will thus appreciate that the association of waves with the expanding S^* surface was the result of mathematical ingenuity, and was made before electrons had been shown to undergo diffraction effects.

Chapter VI.—Wave Equations and Their Interpretation.

We have now to proceed to the final stage of setting up a wave equation and interpreting it in terms of electrons. A beam of electrons of uniform velocity will correspond to a monochromatic ray of our hypothetical mechanical waves, although the velocity u of the electrons is totally different from the velocity $\left(\sim\frac{c^2}{u}\right)$ of the waves; we shall consider later what function of the waves corresponds with the actual velocity of the electrons. The hypothetical "something which vibrates" is denoted by Ψ, and in accordance with the general analogy with the theory of light, the amplitude of the hypothetical Ψ vibrations is a measure of the electron density at the place concerned. A large value of the amplitude of the Ψ vibrations corresponds with a high electron density and a large probability of finding an electron at the place concerned. In expressing this precisely, a difference exists between the optical theory and the wave mechanics. In the electromagnetic theory of light, the state of the vibrating medium is described by two vectors,* E and H, and the intensity of illumination, or the density of photons, is proportional to $(E^2 + H^2)$, and this intensity fluctuates with the time, because E and H are taken to describe waves in phase with one another. In the same way † we may describe the hypothetical Ψ vibrations by two functions f and g, so that the electron density is proportional to the value of $(f^2 + g^2)$ at the place concerned. The wave-mechanics theory is then developed on the assumption that at a given place $(f^2 + g^2)$, and hence the electron density, is independent of time.‡ This implies that f and g must be one-quarter of a period apart. In the very simple case of a plane wave, for example :

if $\quad f = a\cos 2\pi(\nu t - x/\lambda) \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{I (15)}$

then $\quad g = a\sin 2\pi(\nu t - x/\lambda).$

So that $\quad f^2 + g^2 = a^2\,[\cos^2 2\pi(\nu t - x/\lambda) + \sin^2 2\pi(\nu t - x/\lambda)] = a^2.$

* A vector is a quantity which has both magnitude and direction, and a scalar a quantity involving magnitude only. If the radius of a circle revolves like the hands of a clock, the length of the radius is a scalar quantity independent of direction.

† This treatment is taken from "An Outline of Wave Mechanics," by N. F. Mott (Cambridge University Press), with the permission of the author and publisher.

‡ The theory developed in this way because when wave mechanics was invented it was necessary to assume wave functions to describe the phenomena. The essential requirement was a measure of the intensity of electrons in a beam, and it was therefore convenient to adopt a function which made the intensity of a beam independent of the time at any one place.

In this way $(f^2 + g^2)$ is independent of time, and in this very simple case is also independent of the space-co-ordinate x, although in the more general case $(f^2 + g^2)$ varies from place to place.

The method universally employed is to replace the pair of real functions, f and g, by the single complex function :

$$\Psi = f + ig \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{I (16)}$$

where $i = \sqrt{-1}$. The conjugate complex of Ψ which is denoted Ψ^* is equal to $f - ig$, and the electron density is proportional to :

$$f^2 + g^2 = (f + ig)(f - ig) = \Psi\Psi^* \quad . \quad . \quad \text{I (17)}$$

The reader who is not familiar with the use of complex numbers may content himself with noting that the method used is merely a mathematical device for expressing the assumption that the hypothetical Ψ waves are the result of two vibratory processes which are one-quarter of a period apart, and so unite to give a resultant which is independent of time at any one place. The assumption often leads the beginner into difficulties, because there is a natural tendency to think of a wave process as involving a fluctuation with time, but as can be seen from the above example of sine and cosine functions, it is quite possible for two vibratory processes to unite so as to produce a resultant which is independent of the time. In the symbolism of this method, the electron density is proportional to the value of $\Psi\Psi^*$ at the place concerned, and the number of electrons in an element of volume ΔV is proportional to $\Psi\Psi^*\Delta V$. It is helpful to remember that $\Psi\Psi^*$ is real, even though Ψ be complex, and the electron density is always proportional to $\Psi\Psi^*$. In some problems it is possible to express the electron density in other ways, and to understand this the details given in the Appendix (p. 39) must be appreciated.

For a stationary state in which the energy is fixed and equal to $h\nu$, the general form of the function Ψ may be written

$$\Psi(x, y, z, t) = \psi(x, y, z)e^{2\pi i\nu t} \quad . \quad . \quad . \quad . \quad \text{I (18)}$$

where $\psi(xyz)$ is sometimes called the *space factor* or the *amplitude factor*, and $e^{2\pi i\nu t}$ is the *time factor*. This is merely another way of expressing the assumption that the electron density is independent of time, since

$$e^{2\pi i\nu t} = \cos 2\pi\nu t + i \sin 2\pi\nu t \quad . \quad . \quad . \quad \text{I (19)}$$

which is of the form $(f + ig)$ used in the previous description. The scalar value of $e^{2\pi i\nu t}$ is thus unity, though this is not to be taken as

implying that the vibratory process is independent of time; rather is it imagined to be the result of two vibrating processes, each of which fluctuates with time, but which compound so that their resultant, although in the general case varying from place to place, is independent of time at any one place. In equation I (18), ψ is thus the amplitude of Ψ, and Ψ and ψ have the same scalar value, so that as long as we are not concerned with the time, Ψ and ψ are often interchangeable, since they have the same scalar value,† and obey the same differential equations (see below), and the electron density is thus proportional to $\psi\psi^*$.

We have seen that the general problem of the motion of a particle in a variable field of force is analogous to the motion of light rays in a medium of variable refractive index. In general the variation of the potential energy as a function of the space co-ordinates will be known, and the wave equation expressing the magnitude of Ψ first proposed by Schrödinger is of the form:

$$\nabla^2\Psi + \frac{8\pi^2 m}{h^2}(E - W)\Psi = 0 \quad . \quad . \quad . \quad \text{I (20)}$$

Here W is the potential energy and E the total energy, whilst the symbol $\nabla^2\Psi$ stands for $\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right)$ and is sometimes written $\Delta\Psi$ by Continental writers. This equation is known as the First Schrödinger Equation, or the time-free equation, for ordinary (non-relativity) mechanics, and it represents a family of surfaces, each corresponding to one value of E. As explained in the Appendix (p. 39) the amplitude ψ obeys an equation of exactly the same form. In the present book we are not concerned with the mathematical development of these equations, or of the further equation described in the Appendix, but the reader will meet the equations so frequently that the meaning of the symbols should be understood.

In the general type of problem with which we are concerned, the variation of W is known—thus, in the problem of the hydrogen atom the potential energy is equal to $-\frac{e^2}{r}$—and the methods of wave mechanics consist in finding suitable solutions to the appropriate wave equation, and then interpreting these on the assumption that $\Psi\Psi^*$ is proportional to the electron density at the place considered. As we have already explained, so far as the paths traversed are concerned, the effect of the wave mechanics is to reduce the problem of

† It is this which leads to the unsatisfactory position in which symbols for Ψ and ψ are often interchanged, or are not distinguished, so that the reader may find the same symbol with different meanings on adjacent pages of the same book.

the path of a beam of electrons in a field of varying potential to a problem of rays of light in a medium of varying refractive index. Examination of the equations then shows that with a particle of total energy, E, and potential energy, W, the effect of varying W is equivalent to the effect on a light ray produced by a varying refractive index, μ, given by :

$$\mu = \left(1 - \frac{W}{E}\right)^{\frac{1}{2}}$$

In general, wave equations of the above type have large numbers of solutions, and the correct solution has to be chosen so that it represents something which is physically possible. Such solutions may be called acceptable solutions, and in most simple problems they result in the condition that ψ shall be everywhere finite and single-valued, and that both ψ and $\frac{d\psi}{dx}$ shall be continuous. In most cases where the solution represents a stationary state, the conditions to be satisfied result in the wave-length, λ, being simply related to some length which the problem involves. Thus, if we consider an electron contained in a one-dimensional box of length L, acceptable solutions are obtained only for which the wave-lengths are equal to $2L/n$, where n is a whole number.* This in its turn implies that only certain energies can give rise to acceptable solutions, and these energies are naturally interpreted as being those of the stationary states of the older quantum theories, and the whole-number relations which the wave-lengths must obey are naturally regarded as connected with the older quantum numbers. In this way it may be said that quantum numbers and stationary energy states appear in wave mechanics, not as arbitrary postulates imposed on one system of mechanics, but as the inevitable conditions which must be satisfied if the equations are to yield acceptable solutions. It is thus of particular fascination to see how wave mechanics, which by its very nature deals with continuous quantities, results in the introduction of the whole numbers required to explain the quantum phenomena.

* If a stretched wire is set vibrating, a steady vibration (*i.e.*, a stationary state of vibration) can be set up only for wave-lengths which are definite fractions of the length of the wire. The wave-lengths of the various possible steady vibrations are then related by whole numbers. This is a physical vibration, but the mathematics which express the whole number relations are roughly analogous to those which introduce the whole numbers into the above problem of electrons. As previously emphasized, this does not mean that the electron is a physical wave.

Appendix to Chapter VI.

The relations implied by the use of complex quantities may be understood by the usual diagram in which the real and imaginary quantities are plotted at right angles, *i.e.*, one-quarter of a revolution apart, just as the sine and cosine terms in I (15) are one-quarter of a revolution apart. In this case, in Fig. 4, points on the horizontal axis represent the real numbers $(f + 0i)$, whilst those on the vertical axis represent the purely imaginary numbers $(0 + ig)$. The vectors $\overrightarrow{OP}$ and $\overrightarrow{OP'}$ represent the complex numbers $\Psi = (f + ig)$ and $\Psi^* = (f - ig)$, respectively. The length OP equals $\sqrt{f^2 + g^2}$ and is a real number, called the modulus of Ψ, and is written $|\Psi|$. The angle ϕ is called the angle † of Ψ, and to multiply two complex numbers the angles are added and the moduli are multiplied. It will be seen, therefore, that on multiplying $(f + ig)$ by $(f - ig)$ the product will be a point on the horizontal axis, *i.e.*, a real number, of magnitude $f^2 + g^2$, so that ‡ $\Psi\Psi^* = |\Psi|^2$, and in the problems with which we are concerned the electron density may be written as proportional to $|\Psi|^2$.

We have explained above the general form of the function Ψ as given by equation I (18), and have seen how this contains both an amplitude factor $\psi(x, y, z)$ and a time factor $e^{2\pi i\nu t}$. If the time factor is chosen so that Ψ is of the form given by equation I (18), then this equation represents a standing wave if ψ is real, and a progressive wave system if ψ has a suitable complex form. It is common practice to omit the time factor in equation I (18), and the reader will often encounter equations, such as $\psi = e^{ikx}$, described as representing travelling waves, and in such cases it is understood that the time factor is to be added.

As explained on p. 37, the electron density is proportional to $\psi\psi^*$, but in many problems concerning stationary states, ψ is real and $\psi\psi^*$ is identical with ψ^2. In such problems it is possible to draw a graph showing how ψ varies with the distance in a certain direction, and from this graph the electron density can be read off by squaring § the values of ψ. It is only in some problems concerning stationary states that this is possible, and the reader should note that $\psi\psi^*$ and ψ^2 are not always interchangeable, and that the electron density is always proportional to $\psi\psi^*$.

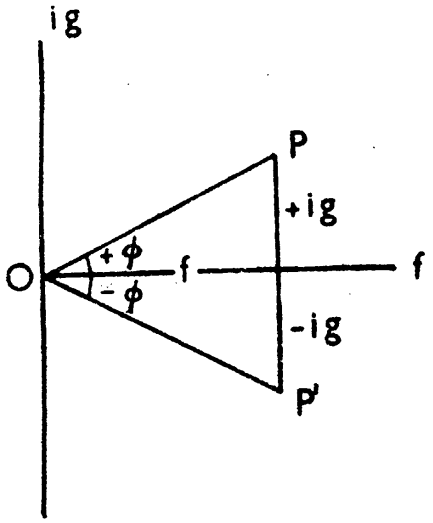


Fig. 4.

The use of imaginary quantities in the above way is merely a mathematical device which reduces some of the equations to a form with which the mathematician is familiar, and when expressed in simple terms the above treatment merely assumes that the hypothetical Ψ vibrations are the result of two vibratory processes, which are one-quarter period apart, and so combine to give a resultant independent of time at any one place.

As stated above, the first Schrödinger equation, I (20), represents a family of

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† This angle is often called the amplitude of the complex number, but we have avoided the use of this expression in order to prevent possible confusion with the amplitude of the Ψ waves.

‡ This is sometimes expressed by saying that the scalar value of Ψ is $\sqrt{f^2 + g^2}$. This is correct, but should not lead one to write Ψ^2 instead of $|\Psi|^2$.

§ Confusion has arisen in many of the books owing to the fact that the description says that the electron density is proportional to $\psi\psi^*$, whilst the examples dealt with are stationary states of the above type, with the result that the beginner is puzzled by the change from $\psi\psi^*$ to ψ^2.

surfaces each corresponding to one value of E. If Ψ is assumed to be of the form given by I (18), the time factor may be cancelled out, and the amplitude equation

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - W)\psi = 0 \quad . \quad . \quad . \quad . \quad . \quad \text{I (21)}$$

is obtained, so that as stated before, both Ψ and ψ obey the same differential equation. If the time factor has the same form as in I (18), the energy E may be eliminated from equation I (21) to yield the Second Schrödinger Equation:

$$\nabla^2\Psi - \frac{8\pi^2 m}{h^2} W\Psi + \frac{4\pi m i}{h} \cdot \frac{\partial \Psi}{\partial t} = 0 \quad . \quad . \quad . \quad . \quad \text{I (22)}$$

This is the more fundamental equation, and can be used for problems where W is an explicit function of the time. Those who wish for further information on the derivation or use of the equations should consult the following books:

Elementary.

Dushman, S. "Elements of Quantum Mechanics." New York: **1928** (John Wiley & Sons, Inc.).
Flint, H. T. "Wave Mechanics." 5th Edn. London: **1946** (Methuen & Co., Ltd.).
Gurney, R. W. "Elementary Quantum Mechanics." Cambridge: **1934** (University Press).
Heitler, W. "Wave Mechanics." Dublin (Dublin Institute for Advanced Studies).
Mott, N. F. "An Outline of Wave Mechanics." Cambridge: **1930** (University Press).

More Advanced.

Frenkel, J. "Wave Mechanics: Elementary Theory." Oxford (Clarendon Press).
Frenkel, J. "Wave Mechanics: Advanced General Theory." Oxford (Clarendon Press).
Pauling, L., and Wilson, E. B., Jr. "Introduction to Quantum Mechanics." New York: **1935** (McGraw-Hill Book Co., Inc.).
Rojansky, V. "Introductory Quantum Mechanics." New York (Prentice and Hall).

Chapter VII.—The Representation of the Individual Electron.

In the preceding description we have dealt with the rays or beams consisting of a continuous stream of electrons, and the wave function was interpreted so that $\Psi\Psi^*\Delta V$ was a measure of the probability of finding an electron in the particular element ΔV concerned. We have next to consider what happens when we try to identify the individual electrons in the stream, and here the interpretation offered is that the total Ψ is regarded as the sum of the effects due to the individual electrons, so that $\Psi\Psi^*\Delta V$ is also proportional to the probability of finding any one particular electron in the volume ΔV. The constant of proportionality is obtained by a process known as *normalization* of the wave function. If, for example, we deal with a problem in which one electron is contained in a volume V, then the integral $\int \Psi\Psi^* dV$ over the whole volume V, must equal one, since the probability that the electron is somewhere in the volume V is clearly unity.

This interpretation of the wave equation as giving the probabilities for one single electron implies naturally that we can no longer regard an electron as being localized at a given point, since all we can know are the probabilities of its being in various small volumes. Similarly, the motion of the electron can no longer be described by expressing the space co-ordinates (xyz) of the electron as a function of the time, but has to be considered in terms of the whole wave function which involves x, y, z, and t. From practical experience we know that what we observe as the electron is confined to a relatively small region of space, and if we are in any way to localize the electron, we must find some function of the hypothetical Ψ waves which has an appreciable amplitude only over a small region. We may understand this by considering how we could isolate a small portion from an infinite monochromatic wave. To do this we might arrange an aperture provided with a shutter which could be opened for a very short time, thus allowing a small group of waves to pass through. In this case, if we are dealing with actual material waves, we find that the action of the shutter slightly disturbs the head and the tail of the wave group, whilst the sides of the aperture disturb the sides of the wave group. The effect of this is to produce a wave group which is not homogeneous, but may be regarded as composed of a large number of slightly different frequencies. The result of this is that the individual waves stream forward with the

phase-velocity U, but that owing to their slightly different frequencies they interfere with one another, and so have a negligible amplitude, except over a small region where they reinforce one another to produce a small wave group, as shown in Fig. 5. The centre of the region in which the amplitude is appreciable moves forward with a velocity u, which is very much smaller than U, and which is given by the equation for the group velocity :

$$u = \frac{d\nu}{d\left(\frac{1}{\lambda}\right)}$$

Since $U \gg u$, the individual waves which reinforce one another to produce the wave packet are continually changing and may be regarded as streaming on through the packet, but the centre of the region in which there is an appreciable amplitude moves on with the much slower group velocity u. Further, as the wave packet moves on, it tends to spread

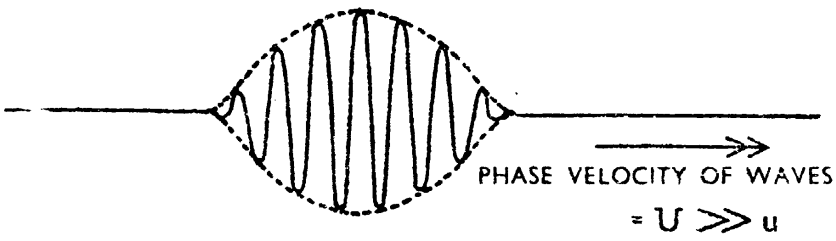


FIG. 5.—Velocity of Centre of Wave Packet = Group Velocity $u = \frac{d\nu}{d(1/\lambda)}$.

out, and this spreading out is more rapid the shorter the group of waves cut out by the shutter, since it will be appreciated that the shorter the wave group, the relatively greater is the disturbing effect produced by the shutter. In the case of the Ψ waves we are dealing with nothing material, but are to interpret the hypothetical waves so that their amplitude is a measure of the probability of finding an electron at the place concerned. If the shutter is opened for such a short time that only one electron passes through, the wave packet of the hypothetical Ψ waves will refer to the one single electron. The wave packet of Ψ waves is thus not to be interpreted as the electron itself, but as representing a limited region of space in which there is an appreciable probability of finding the electron.* That this region of space moves on with the

* We have explained that the Ψ waves are assumed to be the result of two vibratory processes, one-quarter of a period apart, which reinforce one another so that the resultant amplitude does not oscillate with the time, and we should therefore think of the electron wave packet as the envelope shown by the dotted line in Fig. 5, and this envelope moves along with the velocity u.

velocity of the electron is thus understandable,* but the electron may be found at any point within the region represented by the wave packet, the probability being greatest in the region of the packet where the amplitude is greatest.

We have next to consider how we may interpret the spreading out of the wave group referred to above, and it will readily be seen that this is equivalent to an uncertainty in the velocity of the electron. As the wave group spreads out the amplitude diminishes, and instead of a large probability of finding the electron in a very small region of space, we have a probability which is smaller on the average, but extends over a larger region of space, and since there is only one electron this is equivalent to an uncertainty in its velocity. We have seen that the wave-group spreads out more rapidly, the smaller it is at the beginning, and from this it can be seen that the " probability wave-packet " concept expresses the exact characteristics of the Heisenberg Uncertainty Principle. A very small wave packet means that the electron's position is located precisely, because the region in which there is a probability of finding it is very restricted, and under these conditions the probability wave packet spreads rapidly, and the velocity is correspondingly uncertain. If we are asked what process is concerned, we can only reply that if we used any kind of shutter device in order to cut one electron out of a beam, then the movement of the shutter very near to the electron would produce fields slightly disturbing the latter, and the experiment is in fact only an attempt to measure the exact position of the electron, using a shutter instead of the beam of light described on p. 18. If we diminish the size of the aperture, and so diminish the uncertainty in the initial position of the electron in directions at right angles to the beam, we then produce diffraction effects which are equivalent to an uncertainty in the velocity in these directions, since there is now a greater probability of the electron being found moving in a direction different from that of the original beam. It will be seen, therefore, that the probability wave-packet concept has the exact characteristics of the Heisenberg Uncertainty Principle in so far as exact description of the position leads to an uncertainty in the velocity and *vice versa*, and it is easy to show that $\Delta x \times \Delta p \sim h$.

* We can readily see that if for free electrons,

$$\nu = \frac{E_m}{h} = \frac{mc^2 + \frac{1}{2}mu^2}{h}$$

and

$$\frac{1}{\lambda} = \frac{mu}{h},$$

then

$$\frac{d\nu}{d\left(\frac{1}{\lambda}\right)} = u.$$

The above description will show that when we are dealing with the motion of an electron over distances which are very large compared with the wave-length, we may to some extent follow the electron in its path by considering the motion of the probability wave packet, although there is always some uncertainty in the simultaneous position and velocity, energy and time, &c. But this simple visualization breaks down when we consider the motion of the electron over distances comparable with the wave-length. The probability wave packet by its very nature extends over several wave-lengths, but the probabilities indicated by its varying amplitude refer to the one single electron, and this, therefore, cannot be visualized as moving about within the length of the wave packet. Over this small distance all that can be described is the probability of finding the electron in a given small region, and all attempts to follow the electron about in space must be given up. The theory, which is confirmed by experiment, indicates that the "sizes of atoms" (*i.e.*, the regions in which there is an appreciable probability of finding electrons) are of the same order as the wave-lengths of the electrons in the atoms in their normal states, and from the point of view of wave mechanics it is meaningless to speak of electrons "moving in orbits," or try to visualize them as particles "running round" orbits of the circular, elliptical, or rosette types. All that we can obtain is a wave function from which we can evaluate $\Psi\Psi^*$ at different points round the nucleus, and in this way we can visualize the electron in an atom as giving rise to a "probability cloud," or "electron cloud" of varying density, a high density of the electron cloud corresponding to a high probability of finding the electron at the place concerned.† In atoms with more than one electron, the total electron cloud is formed by the summation of the probability clouds of the individual electrons, and some of the details of these electron-cloud patterns will be considered in later chapters. These electron-cloud patterns constitute our "pictures" of the atoms concerned, but the electron-cloud pattern of a given energy state must be accepted as a whole, and no attempt must be made to visualize the electron as moving about within the pattern. If it is asked why this should be so, the answer is that if we speak of an electron moving about within a given energy state, we imply that we can observe it at successive instants, but in any actual experiment the first observation would disturb the electron and remove it to a different energy

† It was here that the early wave mechanics was in error, since it regarded the electron as *being* a wave running round and round an elliptical orbit, whereas the probability interpretation is the correct one, and requires a complete surrender of attempts to follow the electron round the orbit. It is unfortunate that the terms "orbit" and "orbital" from the older theories are often retained in order to describe the electron cloud patterns of the new theories, although in many cases the concept of an orbit is misleading.

state, so that two observations of the same state are impossible. These difficulties of describing events on an atomic scale are merely expressions of the Heisenberg Uncertainty Principle, and the probability interpretation of wave mechanics is the nearest approach we can make to a visualization of electrons over distances of the same order as the size of an atom.

In spite of the fact that an electron in an atom is no longer to be thought of as a particle running round an orbit, an electron state of an atom corresponds with a quite definite angular momentum, which in the hydrogen atom is equal to $\frac{h}{2\pi}\sqrt{l(l+1)}$, where l is a whole number. If it is asked what is meant by angular momentum when we must no longer imagine a particle revolving in an orbit, the answer is that the electron state has associated with it a property which in processes such as collisions behaves analogously to the angular momentum of classical mechanics. If $l = 0$, the angular momentum is thus zero, but this is not to be taken as indicating that the electron is stationary, but rather that its motion is as likely to be in one direction as another, and consequently gives rise to no resultant angular momentum.

Chapter VIII.—The Meaning of Velocity.

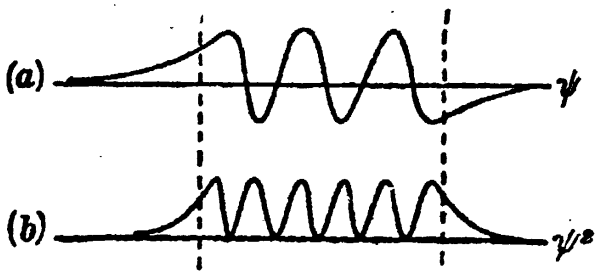
We have seen above how the Heisenberg Principle leads to a degree of uncertainty in the velocity of the electron. Apart from this, the use of wave mechanics introduces a new phenomenon in connection with the motion of a particle in a field of force, which is quite absent from classical mechanics, and which requires a careful definition of exactly what is meant by the term velocity. For simplicity we may deal with motion in one dimension, and in this case the motion of an electron in a field of varying potential is analogous to the passage of a ray of light in a straight line through a medium in which the refractive index varies from place to place, but is constant in any one plane perpendicular to the ray. In the optical problem we know that a certain fraction of the light is transmitted and a certain fraction reflected, the proportion of the reflected light becoming smaller as the wave-length is smaller. Expressed in terms of photons, this means that we cannot say what will happen to an individual photon, but at each place there is a certain probability that its velocity will be reversed in direction. The wave mechanics leads to an analogous effect in the case of an electron moving in a varying potential field, and at each place, although it is impossible to say what will happen to the individual electron, there is a certain probability that the velocity of the electron may be reversed, without change of magnitude. If the wave function Ψ is known, then at any one point $\Psi\Psi^*\Delta V$ is a measure of the probability of finding an electron in the volume ΔV, and a corresponding function can be found which gives the probability of a reversal in direction of the velocity. We have therefore to distinguish carefully between the mean velocity v associated with an electron represented by a given wave function and the root mean square velocity u. If, for example, an electron state is obtained by the superposition of two travelling waves of equal amplitude but moving in opposite directions, we shall have a standing wave for which the mean velocity v is zero, since there is an equal probability of finding the electron moving in either direction, but the root mean square velocity will, of course, have a definite value. In the Brillouin zone theories of electrons in a crystal, this point is of great importance. Here the potential varies greatly over very small distances, and a given factor may affect v and u quite differently; a quite misleading impression may therefore be gained unless it is realized that the mean velocity v takes into account the probability of the reversal of direction of the velocity.

Chapter IX.—Potential Boundaries in Wave Mechanics.

The wave equations in Chapter VI involve the terms $(E - W)$, where E is the total energy (kinetic plus potential) and W is the potential energy. In the problems of the older mechanics, the kinetic energy could only be zero or positive, and so $(E - W)$ was always positive, and regions where $(E - W)$, or the kinetic energy, would be negative were forbidden regions into which the particle concerned could not penetrate. If, for example, a ball were thrown vertically into the air with a given kinetic energy, it would gain potential energy and lose kinetic energy until it came to rest, and the region beyond this point was one into which it could not enter unless additional energy were supplied. In wave mechanics, on the other hand, there is no sharp boundary between permissible and forbidden regions, and a particle has a probability of penetrating into the region where $(E - W)$ is negative, although the probability rapidly diminishes as this region is entered. In the problem of a ball thrown into the air, this effect would be entirely negligible, owing to the small value of Planck's constant, but in problems concerning electrons, the effect often produces interesting results. The wave equations of Schrödinger can be applied to both the region where $(E - W)$ is positive and the region where $(E - W)$ is negative, and the ψ functions in the two regions fit smoothly on to one another. We may illustrate this by considering an electron contained in a one-dimensional potential box, the potential being constant inside the box, but rising sharply at the walls whose positions are shown by dotted lines in Fig. 6. Then, according to the old mechanics, an electron whose kinetic energy was less than the potential step at the boundary was confined to the box, and there was a zero probability of finding it beyond the boundaries. We have already explained that the stationary states of an electron in a one-dimensional box are characterized by wave-lengths such that the length of the box is an integral number of half wave-lengths. Fig. 6 shows a hypothetical ψ pattern with two and a half wave-lengths in the length L. The meaning of this pattern is that if we square the value of ψ at any point, then ψ^2 is proportional to the probability of finding the electron at the point concerned. In this case the solution of the equation shows that in the forbidden region, ψ falls off exponentially, *i.e.*, according to a relation of the type e^{-kx}, where k is very large, so that ψ, and hence ψ^2 and the probability of finding the electron, diminish very rapidly as the for-

bidden region is entered. This figure shows how ψ falls off exponentially as the forbidden area is entered, and the reader will encounter numerous diagrams in which ψ patterns have exponential tails of this kind, instead of the sharp boundary which would exist in classical mechanics. The rapid fall in the exponential curve means that as the forbidden region is entered the probability of finding an electron very soon becomes negligible, and if the potential wall is thick there is little difference between the new and old concepts. But if the thickness of the potential wall is of the same order as the wave-length, very interesting effects are met with, and an electron may penetrate a thin potential wall which it could not surmount according to the older view, this effect being of importance in some problems of electronic emission from metals with surface films (p. 176).

The second curve in Fig. 6 shows the probability of finding the



[*Courtesy, Cambridge University Press.*

FIG. 6.—The upper diagram shows one of the possible ψ patterns for an electron enclosed in a one-dimensional box, whose length, L, is bounded by the dotted vertical lines. The ψ pattern chosen is the stationary state for which the wave-length is equal to $2L/5$. The probability of finding the electron at different places is proportional to ψ^2, and the lower curve shows the curve for ψ^2.

electron in different places across the box.† It will be seen that there are places where this probability is zero, and the question is often asked as to how, if this is so, the electron can travel from one part of the box to another. The answer to this question is that the above " probability pattern " refers to a stationary state of the electron in the box, but if we speak of the electron moving about in the box we imply that we can make successive observations on the electron, and so follow its path. Actually, however, the first observation will disturb the electron, and so remove it from the stationary state concerned. We have thus to accept the probability pattern as giving all that can be known of the electron in the one stationary state. If we wish to consider the electron as travelling about inside the box, we shall have to regard it as a wave packet, smaller than the box itself, and in this case the wave packet will be built up of a group of states,

† The problem is one of a stationary state in which $\psi\psi^*$ is equivalent to ψ^2 (see p. 39), and the second curve is obtained by squaring the ordinates in the first curve.

whose probability patterns will be superimposed. This difficulty is continually met with in dealing with electron-cloud patterns or probability patterns of stationary states, and we have to remember that the probability pattern of a given energy state always implies that the time is completely indeterminate, so that no attempt must be made to follow the electron about within the pattern of the state.

PART II.—THE STRUCTURE OF THE FREE ATOM.

Chapter X.—The Electron Groups.

As we have explained in the preceding chapters it is not possible to give any precise mechanical picture of the motion of the electrons round the positively charged nucleus of an atom. If an atom contains more than one electron, each individual electron moves in the field resulting from the attraction of the nucleus and the repulsion of the other electrons, all of which are in motion. Wave mechanics then gives us for the system as a whole, a number of possible wave functions, and these have to be interpreted on the assumption that $\Psi\Psi^*$ is a measure of the electron density at the place concerned. From this point of view the spatial distribution of the electrons in an atom may be represented by a series of diagrams, each giving the total electron density as a function of the distance from the nucleus in a particular direction. The complete series of diagrams then gives us what may be termed a "probability pattern," representing the electron density in the space surrounding the nucleus, and it is the shape of this pattern which constitutes our "picture" of the atom concerned. To a fairly close approximation we may assume each electron to move in a potential field which represents the attraction of the nucleus and the average of the instantaneous repulsion of all the other electrons. Wave mechanics then gives us for each electron a number of possible wave functions, and the total electron density at a given place is proportional to the sum of the values of $\Psi\Psi^*$ for each of the electrons in the atom.

The electrons in an atom can occupy different energy states, and each electron state in a given atom gives rise to a definite electron cloud pattern, and is characterized by a definite energy, and the first thing to be grasped is the division of the electrons among the main energy groups or quantum shells. These groups are characterized by quantum numbers, and the state of an electron in an atom is described by four quantum numbers, n, l, m_l, and m_s. The precise significance of these is described later (p. 62), and for the moment we may note that, speaking in a general way, the quantum number n is a measure of the energy of the electron in the state concerned, and l is a measure of its angular momentum; l may have any value from 0 to $(n-1)$, but a state where $l = 0$ is not to be regarded as one in which the electron is at rest, but rather as one in which the motion does not

give rise to an angular momentum, and cannot be visualized in terms of "orbits." *

The quantum number m_l is a measure of the component of the angular momentum in a particular direction, which may be taken to be that of an applied magnetic field; m_l may have any value from $+ l$ to $- l$, including 0. As explained later (p. 62), it is really meaningless to speak of the component of the angular momentum in a perfectly free atom, since the term "component" by its very nature implies that there exists some axis with reference to which measurements can be made. The policy usually adopted is to define the z axis as the direction of an applied magnetic field, and then to imagine the field to be reduced until it is vanishingly small. By a free atom we mean, therefore, an atom in which the direction is defined by a very weak magnetic field. In free atoms, electron states with the same n and l, but with different values of m_l, have the same energy and are said to be *degenerate*, this term being used to describe any case in which different wave functions lead to the same energy. When the atom is placed in a weak magnetic field, the degeneracy is removed, and each value of m_l gives rise to a slightly different energy.

The fourth quantum number, m_s, is due to the electron spin (see p. 64). In a magnetic field, the spinning electron can take up either of two directions, and this effect is represented by the spin quantum number m_s, which can assume the two values $\pm \frac{1}{2}$, according to the direction of the spin. In general, the difference between the energies of electrons with a given value of n, l, and m_l, and with $m_s = + \frac{1}{2}$, or $m_s = - \frac{1}{2}$, is very small, but it increases with the atomic number.

In order to avoid the continual printing of expressions such as $(n = 2, l = 1, m = 0)$, it is customary to use the small letters s, p, d, and f to describe electron states for which $l = 0, 1, 2$, and 3, respectively, whilst a large figure before the letter indicates the value of n. The symbol $3d$, for example, stands for a state in which $n = 3$, $l = 2$. If the symbol is enclosed in a bracket with a small superscript number outside, this indicates the number of electrons in the sub-group concerned. Thus the structure of the normal atom of boron may be written $(1s)^2(2s)^2(2p)^1$, which implies that the atom contains two electrons in the $(1s)$ state, two in the $(2s)$ state, and one in the $(2p)$ state.

The *state of an electron* in an atom is thus described by the four quantum numbers n, l, m_l, and m_s, and in a given atom each electron

* In classical mechanics there is an "orbit" corresponding to $l = 0$, namely, oscillation of an electron along a straight line passing through the nucleus, but this kind of motion is clearly impossible, and in the new mechanics the state $l = 0$ should be regarded as one in which the motion is as likely to be in one direction as in another.

state has a definite energy. The energy of the atom as a whole can thus assume a number of different values, according to the way in which its electrons are arranged in the different possible electronic states. Each of these arrangements may be said to give rise to a *state of the atom*,* and the most stable state is that for which the energy is a minimum. This may be referred to as the *normal state* of the atom concerned, and the states of higher energy content are called *excited states*.

It might at first be thought that the normal state of every atom would be such that all the electrons occupied the lowest quantum state. Actually, however, this is not the case, and the facts are summarized by what is known as the *Pauli Exclusion Principle*. According to this Principle no two electrons in an atom can be in exactly the same state as defined by all four quantum numbers. An atom may, for example, have one electron in the state characterized by $n = 1$, $l = 0$, $m_l = 0$, and $m_s = +\frac{1}{2}$, and one electron in the state characterized by $n = 1$, $l = 0$, $m_l = 0$, and $m_s = -\frac{1}{2}$, but only one electron can be in the same state as defined by all four quantum numbers. Since l varies from 0 to $(n - 1)$, and m_l varies from $+ l$ to $- l$, including zero, this implies that the maximum possible numbers of electrons with principal quantum numbers $n = 1, 2, 3, 4, \ldots n$, are $2, 8, 18, 32, \ldots 2n^2$, respectively. This Principle was first put forward empirically, and was later shown to be, if not a logical outcome of the wave mechanics, at any rate in complete agreement with its requirements.†

The Pauli Principle is of very great importance because it applies to all structures in which electrons occupy stationary states characterized by quantum numbers. In all such cases there cannot be more than one electron in each state as defined by all the quantum numbers, including that of the spin. In some treatments it is customary to omit the spin quantum number, and to say that each electron state can contain not more than two electrons; in this case, if a state is fully occupied it will contain two electrons, one of each spin. The difference between these two definitions of the Pauli Principle depends simply on whether the spin quantum number is taken into account in defining an electron state.

The Pauli Principle implies, therefore, that in atoms with several electrons, only two of these can be in the (1*s*) state, and the remainder

* It will be noted that the term "state" is used to describe both the condition of an individual electron in an atom, and the condition of the atom as a whole. In general, the context makes clear the sense in which the word is being used.

† The Pauli Principle is necessitated by wave mechanics if the additional assumption is made that the wave function of the whole system of electrons is completely anti-symmetric in the co-ordinates of the electrons, *i.e.*, on interchanging the co-ordinates of any two electrons the wave function must change its sign.

must be in higher states. The classification of electrons into groups was first made by Bohr, and later extended by Stoner and Main-Smith. For our purpose it is usually sufficient to deal with the main groups and sub-groups described by the first two quantum numbers, and the later division into further sub-groups will not be considered in detail. Table II shows the electronic structures of the free atoms in their normal states, and it must be emphasized that these refer to free atoms, and not to atoms in a liquid or solid.

The characteristics of Table II have been described so often that we shall only refer to them briefly here, and for full details the reader should consult a book such as Sidgwick's " The Electronic Theory of Valency," or Pauling's " The Nature of the Chemical Bond."

The atomic number of an element which gives its order in the table is equal to the number of extra-nuclear electrons in the atom, so that the atom of an element of atomic number Z has a nucleus with a charge of $+ Ze$ surrounded by Z electrons. Hydrogen and helium in their normal states have one and two electrons respectively in the 1-quantum group. By Pauli's Principle this group can contain not more than two electrons which must be of opposite spins, and in the next element, lithium, the third electron enters the 2-quantum shell, and it is this electron which gives rise to the metallic properties. The passage from lithium to neon results in the filling up of this shell to its maximum of 8 electrons. During this process, the electrons first enter the $2s$ sub-group, and beryllium has two ($2s$) electrons with opposite spins. On passing from boron to neon, the electrons fill up the ($2p$) sub-group until this contains six electrons, which is the maximum allowed by Pauli's Principle, since the 2-quantum shell then contains 8 (*i.e.*, 2×2^2) electrons. During the filling up of the p-states, the electrons tend as far as possible not to pair with one another, but to occupy different sub-sub-groups, keeping their spins parallel. Thus, in nitrogen the three p-electrons occupy the three sub-sub-groups ($2p$, $m_l = 0$), ($2p$, $m_l = + 1$), and ($2p$, $m_l = - 1$), and the three electron spins are parallel. In the atom of oxygen there is one more p-electron, and this must pair with one of the above three electrons, leaving the other two unpaired.

The 2-quantum shell is completely filled for neon with atomic number 10, and this element is an inert gas because the outer group of 8 electrons is very stable. On passing to sodium with atomic number 11, the last electron has therefore to enter the 3-quantum shell, and sodium is thus a univalent metal. On passing from sodium to argon, the process is analogous to that occurring between lithium and neon, and the 3-quantum shell is built up to a group of 8. According to Pauli's Principle the 3-quantum shell can contain a maximum of 18

TABLE II.—*Atomic Structures* (1).

Element and Atomic Number.	Principal and Secondary Quantum Numbers.									
n =	1	2		3			4			
l =	0	0	1	0	1	2	0	1	2	3
1 H	1									
2 He	2									
3 Li	2	1								
4 Be	2	2								
5 B	2	2	1							
6 C	2	2	2							
7 N	2	2	3							
8 O	2	2	4							
9 F	2	2	5							
10 Ne	2	2	6							
11 Na	2	2	6	1						
12 Mg	2	2	6	2						
13 Al	2	2	6	2	1					
14 Si	2	2	6	2	2					
15 P	2	2	6	2	3					
16 S	2	2	6	2	4					
17 Cl	2	2	6	2	5					
18 A	2	2	6	2	6					
19 K	2	2	6	2	6		1			
20 Ca	2	2	6	2	6		2			
21 Sc	2	2	6	2	6	1	2			
22 Ti	2	2	6	2	6	2	2			
23 V	2	2	6	2	6	3	2			
24 Cr	2	2	6	2	6	5	1			
25 Mn	2	2	6	2	6	5	2			
26 Fe	2	2	6	2	6	6	2			
27 Co	2	2	6	2	6	7	2			
28 Ni	2	2	6	2	6	8	2			
29 Cu	2	2	6	2	6	10	1			
30 Zn	2	2	6	2	6	10	2			
31 Ga	2	2	6	2	6	10	2	1		
32 Ge	2	2	6	2	6	10	2	2		
33 As	2	2	6	2	6	10	2	3		
34 Se	2	2	6	2	6	10	2	4		
35 Br	2	2	6	2	6	10	2	5		
36 Kr	2	2	6	2	6	10	2	6		

TABLE II (*cont.*).—*Atomic Structures* (2).

Element and Atomic Number.	Principal and Secondary Quantum Numbers.										
n =	1	2	3	4				5			6
l =	—	—	—	0	1	2	3	0	1	2	0
37 Rb .	2	8	18	2	6			1			
38 Sr .	2	8	18	2	6			2			
39 Yt .	2	8	18	2	6	1		2			
40 Zr .	2	8	18	2	6	2		2			
41 Nb .	2	8	18	2	6	4		1			
42 Mo .	2	8	18	2	6	5		1			
43 Ma .	2	8	18	2	6	6		1			
44 Ru .	2	8	18	2	6	7		1			
45 Rh .	2	8	18	2	6	8		1			
46 Pd .	2	8	18	2	6	10		—			
47 Ag .	2	8	18	2	6	10		1			
48 Cd .	2	8	18	2	6	10		2			
49 In .	2	8	18	2	6	10		2	1		
50 Sn .	2	8	18	2	6	10		2	2		
51 Sb .	2	8	18	2	6	10		2	3		
52 Te .	2	8	18	2	6	10		2	4		
53 I .	2	8	18	2	6	10		2	5		
54 Xe .	2	8	18	2	6	10		2	6		
55 Cs .	2	8	18	2	6	10		2	6		1
56 Ba .	2	8	18	2	6	10		2	6		2
57 La .	2	8	18	2	6	10		2	6	1	2
58 Ce .	2	8	18	2	6	10	1	2	6	1	2
59 Pr .	2	8	18	2	6	10	2	2	6	1	2
60 Nd .	2	8	18	2	6	10	3	2	6	1	2
61 Il .	2	8	18	2	6	10	4	2	6	1	2
62 Sm .	2	8	18	2	6	10	5	2	6	1	2
63 Eu .	2	8	18	2	6	10	6	2	6	1	2
64 Gd .	2	8	18	2	6	10	7	2	6	1	2
65 Tb .	2	8	18	2	6	10	8	2	6	1	2
66 Ds .	2	8	18	2	6	10	9	2	6	1	2
67 Ho .	2	8	18	2	6	10	10	2	6	1	2
68 Er .	2	8	18	2	6	10	11	2	6	1	2
69 Tm .	2	8	18	2	6	10	12	2	6	1	2
70 Yb .	2	8	18	2	6	10	13	2	6	1	2
71 Lu .	2	8	18	2	6	10	14	2	6	1	2
72 Hf .	2	8	18	2	6	10	14	2	6	2	2

TABLE II (*cont.*).—*Atomic Structures* (3).

Element and Atomic Number.	Principal and Secondary Quantum Numbers.										
n =	1	2	3	4	5			6			7
l =	—				0	1	2	0	1	2	0
73 Ta .	2	8	18	32	2	6	3	2			
74 W .	2	8	18	32	2	6	4	2			
75 Re .	2	8	18	32	2	6	5	2			
76 Os .	2	8	18	32	2	6	6	2			
77 Ir .	2	8	18	32	2	6	7	2			
78 Pt .	2	8	18	32	2	6	8	2			
79 Au .	2	8	18	32	2	6	10	1			
80 Hg .	2	8	18	32	2	6	10	2			
81 Tl .	2	8	18	32	2	6	10	2	1		
82 Pb .	2	8	18	32	2	6	10	2	2		
83 Bi .	2	8	18	32	2	6	10	2	3		
84 Po .	2	8	18	32	2	6	10	2	4		
85 — .	2	8	18	32	2	6	10	2	5		
86 Em .	2	8	18	32	2	6	10	2	6		
87 — .	2	8	18	32	2	6	10	2	6		1
88 Ra .	2	8	18	32	2	6	10	2	6		2
89 Ac .	2	8	18	32	2	6	10	2	6	1	2
90 Th .	2	8	18	32	2	6	10	2	6	2	2
91 Pa .	2	8	18	32	2	6	10	2	6	3	2
92 U .	2	8	18	32	2	6	10	2	6	4	2

electrons, but the group of 8 has a provisional stability, with the result that argon is an inert gas, and on passing to the next element potassium, the new electron enters the 4-quantum shell, and potassium is a univalent metal. From potassium to calcium the process is analogous to that occurring between sodium and magnesium, but on passing to scandium the additional electron does not enter the 4-quantum or valency shell, but enters the 3-quantum shell, and, as can be seen from Table II, the passage from scandium to copper results in the expansion of the 3-quantum shell from a group of 8 electrons to one of 18. These elements are known as the Transition Elements, and are all of variable valency, and this is to be taken as implying that at this stage in the Periodic Table, the energies of the electrons in the $3d$ and $4s$ states are not very different. Similar transition processes occur in the later Periods, although as will be seen from Table II, the exact details of the process are not always the same. It must again be emphasized that the electronic structures given in Table II refer to the free atoms, and not to the atoms in a solid or liquid. Thus, in the

case of nickel the outer electronic arrangement in the free atom is $(3d)^8(4s)^2$, but in solid nickel there are on the average 9·4 electrons per atom in 3*d* states, and only 0·6 per atom in 4*s* states. There has been an unfortunate tendency in some metallurgical papers to assume that the finer details of Table II apply to the atoms in a solid metal, whereas this is not so.

By Pauli's Principle, the 4-quantum shell can contain 32 electrons, and although the group of 18 which is completed at palladium has a provisional stability, it expands later into a complete group of 32. This process takes place in the group of elements known as the Rare Earths which lie between lanthanum and hafnium in the Periodic Table, and is immediately followed by the building up of the 5-quantum shell into a group of 18, and in each Period the elements of Group Ib, copper, silver, and gold, are univalent elements with one valency electron outside a group of 18. On passing from copper to krypton, silver to xenon, and gold to emanation, the changes in electronic structure are similar to those occurring on passing from lithium to neon. In each case a sub-group of two *s*-electrons is first formed, and then the sub-group of six *p*-electrons is built up. One point of great importance is the stability of the sub-group of two *s*-electrons, which increases with the number of the Period. Aluminium does not give rise to a stable Al^+ ion, but, in the third Long Period, the stability of the $(6s)^2$ sub-group is so great that thallium forms univalent thallous salts which are more stable than the trivalent thallic salts, and similarly lead forms divalent salts in which the $(6s)^2$ sub-group persists unchanged. The existence of this stable $(6s)^2$ sub-group is of considerable interest in the study of alloys, because its stability is so great that it persists unchanged in some alloys, although in other alloys the sub-group breaks down. With indium and tin, there is a considerable tendency for the $(5s)^2$ sub-group to persist as a stable sub-group, but with gallium and germanium the stability of the $(4s)^2$ sub-group is not so great.

The energies necessary to remove one, two . . . &c., electrons from an atom are known as the first, second . . . &c., *ionization potentials* of an atom, and it is instructive to see how these vary for the elements of the first Short Period. The data are summarized in Table III, and it will be seen that the ionization potential for the removal of the first electron from a free atom of lithium is only 5·37 v., whilst the removal of the second electron, which involves the breaking up of the completed $(1s)^2$ group requires 75·28 v. Part of this increase is due to the fact that the second electron is being removed from a positive ion instead of from a neutral atom, but as will be appreciated from what follows the greater part of the increase is due to the stability of

TABLE III.

Element.	Ionization Potential, volts.	Transition.	Resulting Electronic Structure.
He	1st 24·465	$He \longrightarrow He^+$	$(1s)^1$
Li	1st 5·37	$Li \longrightarrow Li^+$	$(1s)^2$
	2nd 75·28	$Li^+ \longrightarrow Li^{++}$	$(1s)^1$
Be	1st 9·28	$Be \longrightarrow Be^+$	$(1s)^2(2s)^1$
	2nd 18·12	$Be^+ \longrightarrow Be^{++}$	$(1s)^2$
	3rd 153·1	$Be^{++} \longrightarrow Be^{+++}$	$(1s)^1$
B	1st 8·28	$B \longrightarrow B^+$	$(1s)^2(2s)^2$
	2nd 25·0	$B^+ \longrightarrow B^{++}$	$(1s)^2(2s)^1$
	3rd 37·75	$B^{++} \longrightarrow B^{+++}$	$(1s)^2$
	4th 258·1	$B^{+++} \longrightarrow B^{++++}$	$(1s)^1$
C	1st 11·217	$C \longrightarrow C^+$	$(1s)^2(2s)^2(2p)^1$
	2nd 24·27	$C^+ \longrightarrow C^{++}$	$(1s)^2(2s)^2$
	3rd 47·65	$C^{++} \longrightarrow C^{+++}$	$(1s)^2(2s)^1$
	4th 64·22	$C^{+++} \longrightarrow C^{++++}$	$(1s)^2$
	5th 389·9	$C^{++++} \longrightarrow C^{+++++}$	$(1s)^1$

These figures are taken from Bacher and Goudsmit: "Atomic Energy States" (McGraw-Hill Publishing Co., Ltd.).

the completed $(1s)^2$ group. The first ionization potential of beryllium is 9·28 v., and is thus greater than that of lithium. This is the result of the increased nuclear charge in the case of beryllium. A valency electron of beryllium is not subject to the full attraction of a nucleus of charge $+ 4e$, because part of the attraction is neutralized or screened by the other electrons of the atom. This screening action is due mostly to the electrons of the underlying quantum shells, *i.e.*, the $1s$, electrons in the case of beryllium, but also to a slight extent to the electrons of the same group as the one considered. The second ionization potential of beryllium is 18·12 v., and is thus roughly double that of the first ionization potential. This increase is due almost entirely to the fact that the electron is being removed from a positive ion instead of from a neutral atom. The third ionization potential of beryllium is no less than 153·1 v., and this enormous increase is due to the fact that the removal of the third electron involves the breaking up of the stable $(1s)^2$ group. Examination of the data for boron and carbon will show that there is a similar large increase at the stage which involves the breaking up of the $(1s)^2$ group.

Reference to Table III will show that the first ionization potential of boron is less than that of beryllium, in spite of the fact that the atomic number of boron is the greater. This is because the $(2s)$ sub-group can contain not more than two electrons, and the third electron must therefore

be in a (2*p*) state. The second ionization potential of boron is greater than that of beryllium, since both involve the removal of a (2*s*) electron, and as the screening effect of one (2*s*) electron upon another is relatively slight, the increased nuclear charge in boron attracts each of the (2*s*) electrons in B^+ more strongly than the nucleus attracts the single (2*s*) electron in Be^+.

The data for carbon illustrate the same general principle. The first ionization potential of carbon is greater than that of boron on account of the greater nuclear charge. The second ionization potentials involve the removal of a (2*p*) electron from C^+, and of a (2*s*) electron from B^+, and consequently the energy required is less for carbon than for boron. The third ionization potentials, on the other hand, involve the removal of 2*s* electrons from both C^{++} and B^{++}, and the increased nuclear charge makes itself felt, and the energy required is greater for carbon than for boron. Increasing nuclear charge thus leads to a general increase in the firmness with which electrons are bound to the atoms, although this increase is not smooth and continuous, but is modified by the extent to which the nuclear charge is screened by the different electrons. In some theoretical treatments a screening constant *S* is used, of such a nature that if *Ze* is the nuclear charge, the effective charge for the electron considered is $(Z - S)e$. It is to be noted that the screening constant *S* is not an absolute quantity applicable to all problems. If, for example, a term of the nature $(Z - S)e$ is used to calculate the ionization potential of the electron concerned, the value of *S* required to give the correct result may be different from that needed when a term of the form $(Z - S)e$ is used to calculate some other property.

It must be emphasized that the above figures refer to the free atoms, and are not a measure of the work required to remove an electron from an atom in a solid or liquid metal. The general principle, however, still applies in the sense that increased nuclear charge leads to a firmer binding, modified by the screening effect.

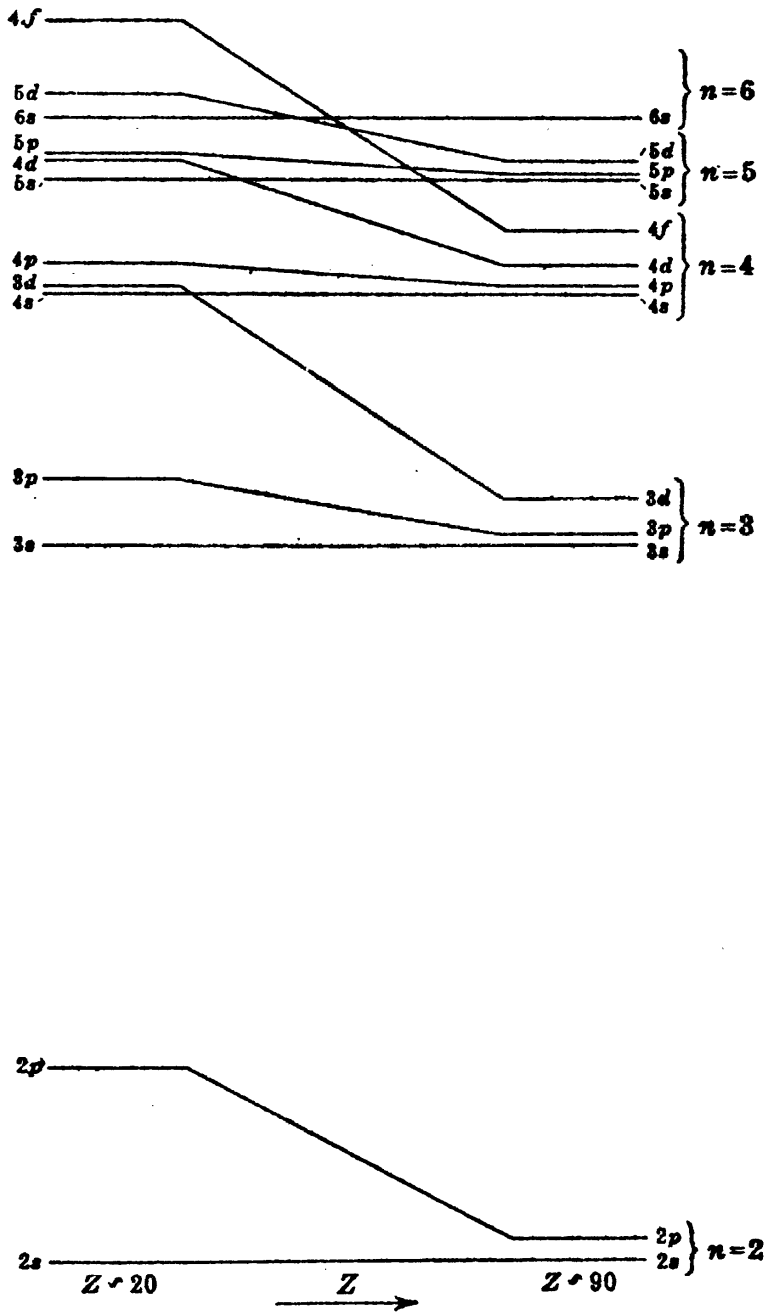
As will be seen from Table II, the 2-quantum shell of electrons is completely filled for neon with atomic number 10, and this element is therefore an inert gas. On passing to the next element, sodium, the additional electron enters the (3*s*) sub-group of the third quantum shell. The first ionization potentials of these atoms are as follows:

Atom.	1st Ionization Potential.
O	13·55
F	18·6
Ne	21·47
Na	5·12

They illustrate clearly how the firmness of the binding of the electrons is affected. From oxygen to neon there is a steady increase in the

ionization potential as the stable $(2s)^2(2p)^6$ group of 8 electrons is built up. On passing to sodium there is a marked fall in the 1st ionization potential, which now corresponds with the removal of a $3s$ electron. The single $(3s)$ valency electron of sodium is thus bound comparatively weakly, and we again have a metallic element. A similar change in the first ionization potential occurs between each inert gas and the following alkali metal. In every case the first ionization potential of an alkaline earth metal is greater than that of the preceding alkali metal, and that of a Group IIB metal is greater than that of the preceding Group IB metal, although the differences are not so marked as those shown above for lithium and beryllium, because the relative change in the screening constants between successive elements tends to become less with increasing atomic number. Thus, the first ionization potentials of potassium and calcium are 4·32 and 6·09 v., respectively, and those of copper and zinc are 7·68 and 9·36 v., respectively. For the transition elements relations between the ionization potentials are naturally more complicated.

The structures of the free atoms are conveniently summarized in Table II, and when it is desired to go into more exact details the energies of the different electrons in an atom may be represented on a scale, so that the distance between two points is a measure of the difference in the energy of electrons in the two states concerned, and is consequently proportional to the frequency of the light emitted when an electron drops from the state of higher to the state of lower energy. In any one atom, for a given value of n, the energies increase in the order s, p, d, f, *i.e.*, with increasing l. For each of the s, p, d, f states, the energy increases with n. In any one free atom, an ns electron always has a higher energy than an $(n-1)p$ electron, so that as far as the s and p electrons are concerned, the energies of the electrons in any one atom increase regularly in the order $1s$, $2s$, $2p$, $3s$, $3p$, . . . For the d electrons the relations are more complicated. We have seen how, in the transition elements, increasing atomic number results in the electrons entering the $(n-1)d$ shell, instead of the np shell. Expressed in terms of energies, this implies that for these elements the energy of an $(n-1)d$ electron is less than that of an np electron, and this is always so when the electrons in the outer shells of an atom are considered. This point is shown clearly in Fig. 7, which gives an approximate representation of the energies of the different electron shells as a function of the atomic number. From this it will be seen that in the transition elements of the First Long Period, the energies of the different shells of electrons are in the order $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, whilst the $4p$ state is unoccupied. In these elements, therefore, the



[*Courtesy, Prentice-Hall, Inc.*

FIG. 7.—Rough Representation of the Relative Energies of the shells for different Nuclear Charge Z (to explain the filling up of inner shells). The elements potassium, rubidium, and cæsium at the beginning of the Long Periods have atomic numbers 19, 37, and 55, respectively. The figure is highly diagrammatic, and over-simplified, and is intended only to show the relative order of the shells. In an accurate diagram the lines would not be horizontal or straight lines, but the relative order would be maintained; the energy decreases on passing from the top to the bottom of the diagram, and the 1*s* states lie too low down to be shown.

outermost ns electron has a lower energy than the $(n-1)d$ electron. In the elements of higher atomic number, where the 3-quantum shell is further down in the atom, this position is reversed, and, as can be seen from the crossing of the lines in Fig. 1, the 3*s*, 3*p*, and 3*d* electrons

all have lower energies than any of the 4-quantum sub-groups. Similar relations apply to the other transition elements. In Fig. 7 the rare earth elements correspond to the position at which the energies of electrons in the $4f$ sub-group have fallen below those of the $6s$ and $5d$ sub-groups, so that with increasing atomic number electrons enter the $4f$ group until this is completed.

Note on the Exact Meaning of Quantum Numbers.

The quantum number n of the new theories replaces the n of the Bohr theory, and even though we drop the idea of an orbit, n retains some of the older characteristics. In the hydrogen atom the negative energy still varies inversely as n^2, so that energy has to be given to an electron to excite it from a state of lower to one of higher n. From the older viewpoint a large value of n implied a large orbit, and from the new point of view it implies that the electron cloud pattern extends over a large region of space.

The quantum number l is a measure of the angular momentum of the electron apart from its spin, and this is called the *orbital angular momentum*, because it corresponds with the angular momentum of the orbit in the old sense. The orbital angular momentum of a hydrogen-like atom is of magnitude $\frac{h}{2\pi}\sqrt{l(l+1)}$, as compared with the postulate of the Bohr theory that the angular momentum was of magnitude $\frac{kh}{2\pi}$. The quantum number l is numerically equal to $(k-1)$ of the Bohr theory, and the occurrence of terms of the type $\sqrt{l(l+1)}$ has led to a confusing position in which the symbol l, sometimes modified by an asterisk, is often printed with the understanding that it must be replaced by $\sqrt{l(l+1)}$ for purposes of calculation.

The third quantum number m_l is a measure of the component of the orbital angular momentum in a particular direction, and to understand its meaning we have to consider what is implied when we speak of the orientation of an atom. In the early stages of atomic theory, where an atom was regarded as a hard sphere, the orientation of an atom had little meaning, but in the new theories the electron clouds are not of uniform density, and are not necessarily of spherical symmetry. When we speak of the shape or orientation of an atom we have to imagine some axis with reference to which a measurement can be made. In a sense, therefore, it is meaningless to speak of the orientation of a perfectly free atom, since the orientation only acquires a meaning when an experiment has been made with reference to some axis. It is convenient to define the z axis as the direction of an applied magnetic field, and then to imagine that the field is gradually reduced to zero, so that when we speak of the orientation of a free atom we really mean an atom as defined by a very weak magnetic field. This point is important because in some cases it determines the exact mathematical treatment to be used.

We have already explained that the Indeterminancy Principle prevents us from knowing simultaneously the angular momentum of a particle revolving round a fixed point and the angle ω made with some fixed reference line by the line joining the particle to the fixed point. The theory then works out in such a way that we may know simultaneously the magnitude of the total angular momentum M, which in a hydrogen-like atom is equal to $\frac{h}{2\pi}\sqrt{l(l+1)}$, and the component of the orbital angular momentum along the z axis which

is equal to $\frac{h}{2\pi}m_l$. We may not, however, know the components in the directions of the x and y axes. The third quantum number m_l then indicates that in a hydrogen-like atom, the component of the orbital angular momentum along the z axis is equal to $\frac{h}{2\pi}m_l$. The quantum number m_l is sometimes called the magnetic quantum number. The orbital angular momentum $\frac{h}{2\pi}\sqrt{l(l+1)}$ is associated with a magnetic * moment whose component along the z axis is equal to :

$$\frac{e}{2mc}\cdot\frac{h}{2\pi}m_l = \frac{eh}{4\pi mc}\cdot m_l.$$

This unit of magnetic moment $\frac{eh}{4\pi mc}$ is called the *Bohr Magneton*, and is equal to $0{\cdot}918 \times 10^{-20}$ erg gauss^{-1}.

The reader will sometimes find this subject described in conjunction with a diagram of the type shown in Fig. 8, with a statement that the angular momentum is in the direction OP, which precesses round the z axis, the angle θ being defined by $\cos\theta = \frac{m}{\sqrt{l(l+1)}}$. This method of representation is to be avoided, because it easily gives the impression that at any instant the angular momentum can be identified with a particular direction OP, whereas as we have explained above, we can never know simultaneously the magnitude of the total angular momentum and of the three components parallel to the x, y, and z axes, respectively. This kind of diagram has survived as the result of attempts to describe the conclusions of the new theories in terms of the old ideas of electrons in definite orbits, but these nearly always lead to inconsistencies at some point. Thus, the electron-cloud pattern of the $2p$ state with $m_l = 1$ has the form shown in Fig. 21 (p. 77), and the density is greatest in the xy plane. The natural interpretation of this from the older viewpoint would be an orbit in the xy plane, so that the motion was confined to this plane. In this case the angular momentum would be perpendicular to the xy plane, *i.e.*, parallel to the z axis, and the total angular momentum and its component parallel to the z axis would be the same, whereas they should be in the ratio $\sqrt{l(l+1)} : m_l$. From Fig. 21 we can see that although the electron cloud is densest in the xy plane, it is not confined to this plane, and this may be interpreted as implying that the motion of the electron is not confined to the xy plane, but includes also motion in other directions. The motion in these other directions gives an average component of the angular momentum along the z axis, although this average component is clearly less than the total angular momentum resulting from these motions.

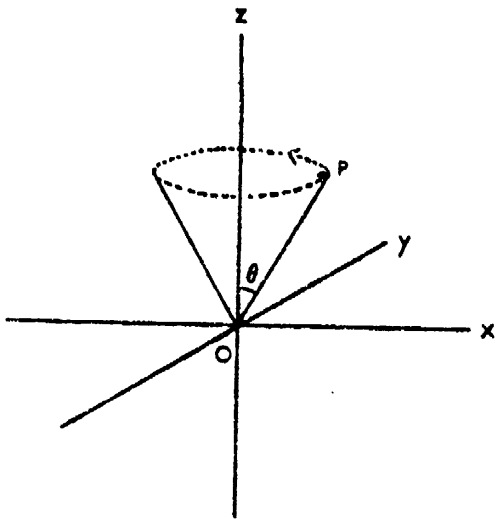


FIG. 8.

Fig. 8 is thus misleading in suggesting that the total angular momentum

* The symbol m in the term $\frac{e}{2mc}$ is, of course, the mass of the electron and not the quantum number m.

can ever be associated with a definite direction OP, but the total orbital angular momentum is to be regarded as rotating round the z axis, and positive and negative values of m_l imply rotation in opposite directions. It is this rotation which is concerned in the so-called *Zeeman Effect* in which the application of a magnetic field causes a splitting of the spectral lines.

The more detailed study of atomic spectra showed that all the facts could not be accounted for by means of the three quantum numbers n, l, and m_l. This difficulty was overcome by Uhlenbeck and Goudsmit, who assumed that the electron has a rotatory motion or spin such that the angular momentum of the spinning electron is of magnitude $\frac{h}{2\pi}\sqrt{s(s+1)}$, where $s = \frac{1}{2}$. The effect of the spin is to introduce a fourth quantum number, m_s, which can assume the two values $\pm\frac{1}{2}$. The component of the magnetic moment along the z axis is $\frac{e}{mc}\cdot\frac{h}{2\pi}\cdot m_s$. The ratio of the magnetic moment of the spinning electron to the angular momentum of the spin is thus $\frac{e}{mc}$, and is double the corresponding ratio of the orbital angular momentum and its associated moment, which, as can be seen from p. 63, is $\frac{e}{2mc}$.

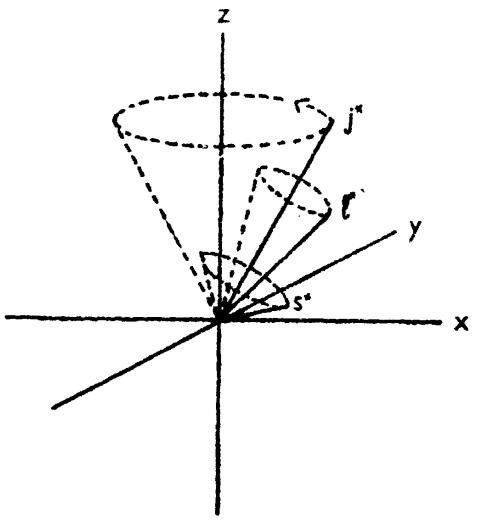


FIG. 9.

It is customary to relate the total angular momentum of the electron to a new quantum number j, such that $j = l \pm \frac{1}{2}$, except that when $l = 0$, only $j = +\frac{1}{2}$ is taken. The magnitude of the total angular momentum is then $\frac{h}{2\pi}\sqrt{j(j+1)}$, and the component in the direction of the z axis is $\frac{mh}{2\pi}$ where the quantum number m takes the values of $\pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}, \ldots \pm j$, so that m is always a half integer, whereas in the simple theory it is a whole number.

The total angular momentum, j, is thus compounded of the orbital angular momentum and the spin momentum, and the condition of affairs is often represented by a diagram of the type shown in Fig. 9, where for abbreviation s^*, l^*, and j^* are written for $\sqrt{s(s+1)}$, $\sqrt{l(l+1)}$, and $\sqrt{j(j+1)}$, respectively, and the angle θ, made by j^* with the z axis, is given by $\cos\theta = m/\sqrt{j(j+1)}$. When the atom is placed in a weak magnetic field, j^* precesses round the z axis. At the same time s^* and l^* precess round their resultant j^*; this precession is due to the interaction between the spin and the "orbit," and takes place in the absence of an external field. In a weak magnetic field the rate of precession of j^* round the z axis is very much slower than the precessions of s^* and l^* round j^*. When the field becomes so strong that the frequencies of these precessions are of the same order the process becomes more complicated, but in still stronger fields it becomes simple again, and the so-called *Paschen-Beck effect* is observed, but these effects lie outside the present work. The use of this kind of figure is open to the same objections as was Fig. 8, and the Heisenberg Principle again prevents us from ever knowing the direction of j^* at a particular instant, although we may speak of a rotation of the angular momentum about the z axis. Since j^* is never completely

determined, it is even more difficult to visualize the precession of s^* and l^* round j^*, and one can only say that the axes of the cones of s^* and l^* are rotating about the z axis, but must never be regarded as being at a particular place.

The reader should also note that there are symbols for describing the electronic state of an atom as a whole, as distinct from the state of a single electron. For these, reference may be made to Bacher and Goudsmit's "Atomic Energy States," and White's "Introduction to Atomic Spectra."

Chapter XI.—Methods of Representation of the Electron-Cloud Density.

In the preceding chapter we have seen how the electrons in the free atoms are divided into groups and sub-groups, each electron being characterized by a definite energy. We have next to consider how the electrons are distributed in space round the nuclei of the different atoms. The problem of the hydrogen atom is naturally the most simple, and since the potential energy of an electron of charge $-e$, moving in the field of a nucleus of charge $+e$, is $-e^2/r$ (see p. 11), the problem of the motion of an electron of total energy E round the nucleus is equivalent to an optical problem involving the passage of light in a spherical bowl in which the refractive index varies in such a way that as the light travels outwards from the centre of the sphere it tends to be bent back again, and does not escape, but remains travelling in a restricted volume. The mathematical treatment is then made more easy by transferring from rectangular to polar co-ordinates, in which the position of a point is described in terms of its distance (r) from the origin, and the two angles θ and ϕ, as shown in Fig. 10. It is then found that the wave function can be split up into a product of three functions $R(r)$, $\bar{\Theta}(\theta)$, $\Phi(\phi)$, which involve only r, θ, and ϕ, respectively. That is to say, $R(r)$ is a function only of r, and does not involve θ or ϕ, and similarly for $\bar{\Theta}(\theta)$ and $\Phi(\phi)$. The probability of finding the electron in any element of volume ΔV is then proportional to the value of:

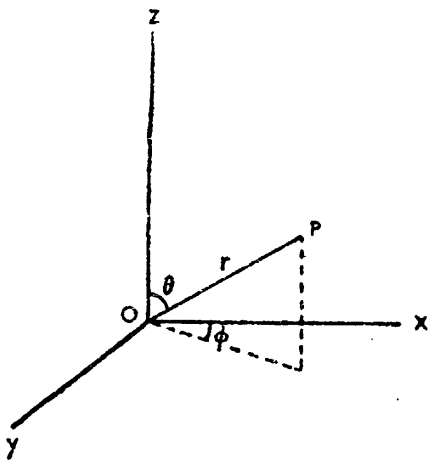


Fig. 10.—To illustrate polar co-ordinates. The position of the point P is given by the length (r) of OP, the angle θ made by OP with the z axis, and the angle ϕ made by the projection of OP on the xy plane with the x axis.

$$\Psi\Psi^*\Delta V = [R(r)R^*(r)] \times [\bar{\Theta}(\theta)\bar{\Theta}^*(\theta)] \times [\Phi(\phi)\Phi^*(\phi)]\Delta V$$

at the place considered, where $R^*(r)$, $\bar{\Theta}^*(\theta)$, and $\Phi^*(\phi)$ are the conjugate complexes of $R(r)$, $\bar{\Theta}(\theta)$, and $\Phi(\phi)$, respectively. This means that the electron density at any point in the atom can be expressed as the product of three terms, one of which involves only the distance (r) from the nucleus, whilst the other two involve only the angles

θ and ϕ, respectively. We have already explained (p. 38) how it is necessary to choose acceptable solutions of the wave equation, and the mathematical treatment then shows that the equation for $\Phi(\phi)$ only yields acceptable solutions if a certain parameter m is equal to $0, \pm 1, \pm 2, \ldots$ &c. When m has been given a particular value, it is found that the equation for $\Theta(\theta)$ only yields acceptable solutions by the introduction of a whole number l, which enters in the form $l(l+1)$, and may have any value (numerically) greater than m, or equal to m. Finally, on introducing values for m and l, it is found that the equation for $R(r)$ only yields acceptable solutions by the introduction of a third whole number n, which must not be less than $(l+1)$. In this way the solution of the wave equation for the hydrogen atom leads to the introduction of the three whole numbers, n, l, and m, and it can be shown that these are equivalent to the quantum numbers n, l, and m_l described in the preceding chapter. This is an example of the fact mentioned in Chapter VI that in wave mechanics, quantum numbers appear, not as arbitrary assumptions imposed on the system, but as conditions which must be satisfied if satisfactory solutions are to be obtained.

In the case of atoms containing more than one electron, the problem becomes extremely complicated, but approximate solutions have been obtained in many cases by the methods of the so-called "self-consistent field." We may illustrate the principle by considering the helium atom, which contains two electrons. For this we may assume that the nucleus of charge $+2e$, and one of the electrons (No. 1) give rise to a particular field, and we may investigate the behaviour of the second electron (No. 2) in this field. The resulting wave functions for electron No. 2 may then be used to calculate the field in which electron No. 1 would move, and then the field resulting from this motion of electron No. 1 may be compared with that originally assumed at the beginning of the calculation, and if there is not a good agreement the whole process must be repeated until the results are self-consistent. Atoms containing more than 50 electrons have been dealt with approximately by these methods, and some of the results will be referred to later.

In the case of the hydrogen atom the value of $\Psi\Psi^*\Delta V$ gives the probability of finding the one electron in the volume ΔV at the place considered, and in the case of other atoms the total electron density is given by the sum of the values for the individual electrons. As explained on p. 44, the picture of the atom which we obtain is that of an electron cloud or probability pattern in which increasing density of the cloud implies a greater probability of finding an electron at the place concerned. It is customary to express the form of the probability

patterns in two ways. The first of these involves the so-called radial electron density $U(r)$, which is defined so that $U(r)dr$ is the number of electrons contained in a spherical shell of radius r and thickness dr. Curves of this kind show the probability of finding an electron at different distances from the nucleus. Such curves are often very useful provided that the definition of $U(r)$ is borne in mind, but they are easily misleading, and must never be taken to indicate the density of the electron cloud of the atom. Since the surface of a sphere of radius r is equal to $4\pi r^2$, a given number of electrons per unit volume implies a value of $U(r)$ which becomes continually smaller as r decreases, and consequently $U(r)$ is very small near the centre of the atom, even though the electron density may be very great.

The second method of expressing the results is in terms of ρ, the charge per unit volume. In atoms whose electron clouds are spherically symmetrical, $U(r)$ and ρ are connected by the simple relation:

$$\rho = \frac{U(r)}{4\pi r^2},$$

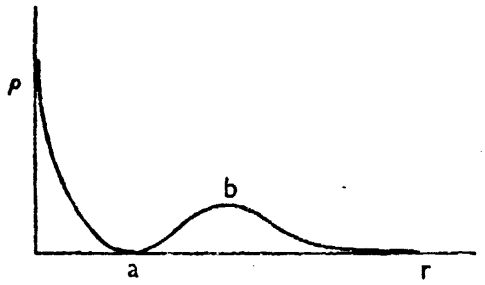


FIG. 11.

and for some purposes it is therefore more convenient to express results in terms of $4\pi\rho$, instead of in terms of ρ itself. In these spherically symmetrical atoms the electron-cloud density can be expressed by a single curve showing the variation of ρ with r.

Thus a curve of the form shown in Fig. 11 represents a spherically symmetrical ball of negative electricity, the density of which diminishes to a value of zero at the distance $r = a$ from the nucleus, rises to a maximum at a distance $r = b$, and then gradually falls away to zero. The point a in Fig. 11 thus corresponds with a spherical node.*

In atoms whose electron clouds are not spherically symmetrical, the relations between ρ and r are different in different directions. It is therefore very difficult to obtain a satisfactory picture of the electron-cloud density, since the electron cloud itself occupies three dimensions, and a fourth dimension is required in order to show the electron density. To surmount this difficulty, use is made of the fact that the wave equation can be split up into the three components $R(r)$, $\Theta(\theta)$, and $\Phi(\phi)$, which involve only r, θ, and ϕ, respectively, the complete electron

* A node is a point at which the amplitude of a vibration is zero, and hence a node implies that no electrons are present at the place concerned. A spherical node thus implies that the atom contains a spherical shell in which there is no chance of finding an electron, although an electron may be found both inside and outside the spherical node.

density ρ being proportional to the product

$$[R(r)R^*(r)][\Theta(\theta)\Theta^*(\theta)][\Phi(\phi)\Phi^*(\phi)].$$

The first term, which may be called the radial probability factor, or the radial density factor, depends on r only, and is therefore spherically symmetrical, and can be expressed in the form of a graph such as that shown in Fig. 12(a). The values of the second term $\Theta(\theta)\Theta^*(\theta)$ can then be expressed in the form of so-called Polar Diagrams of such a nature that if a straight line is drawn from the origin at an angle θ, and cuts the curve of the diagram at the point P, then the length of OP is proportional to the value of $[\Theta(\theta)\Theta^*(\theta)]$ for the value of θ concerned. A diagram of this kind is shown in Fig. 12(b), and for this particular example it will be seen that OP has maxima at $\theta = \pm \pi/2$,

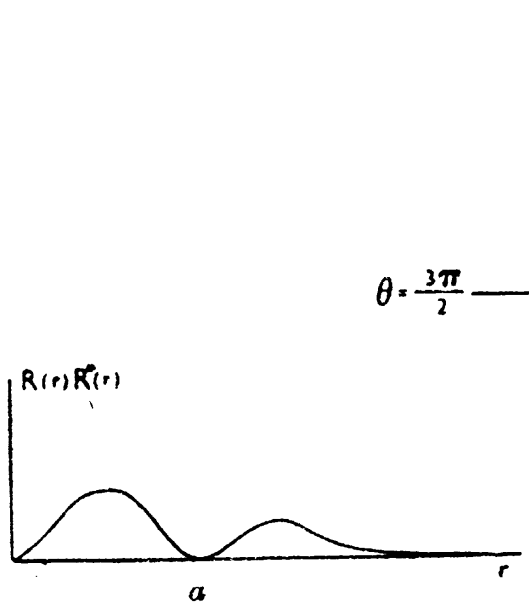


Fig. 12(a).

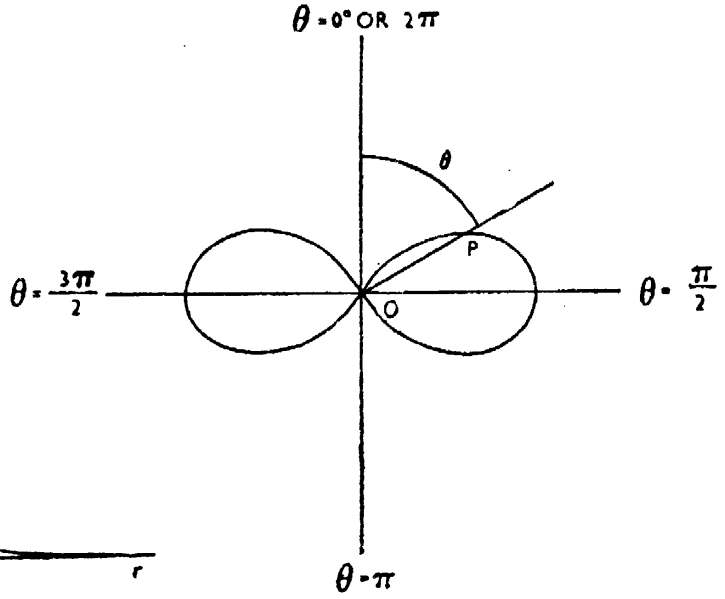


Fig. 12(b).

and is equal to zero for $\theta = 0$ or $\theta = \pi$. Since the total electron-cloud density is proportional to $OP \times R(r)R^*(r) \times \Phi(\phi)\Phi^*(\phi)$, the polar diagram of Fig. 12(b) means that the electron-cloud density is zero along the z axis, because this axis corresponds with $\theta = 0$. A similar 2-dimensional diagram can be drawn to show the variation of $\Phi(\phi)\Phi^*(\phi)$ with ϕ, and the actual electron density at a point with co-ordinates (r, θ, ϕ) is then obtained by multiplying the value of the radial probability factor at the distance r by $OP_\theta \times OP_\phi$. The student has thus to learn to visualize the electron-cloud density in the space surrounding the nucleus as the product of three terms, involving r, θ, and ϕ, respectively. This visualization is difficult, and the process may be made easier by combining the two 2-dimensional diagrams referring to θ and ϕ into a single 3-dimensional polar diagram such

that if a straight line is drawn from the origin at an angle (θ, ϕ) and cuts the surface of the diagram at the point P, the length of OP is proportional to the value of $[\Theta(\theta)\Theta^*(\theta) \times \Phi(\phi)\Phi^*(\phi)]$ for the direction concerned. Fig. 13 shows a three-dimensional diagram of this kind for the case in which the variation with θ is similar to that of Fig. 12(*b*), and in which the value of $\Phi(\phi)\Phi^*(\phi)$ is a constant independent of ϕ. Since in this particular example we have assumed $\Phi(\phi)\Phi^*(\phi)$ to be a constant, the electron density will be independent of ϕ and the figure must therefore be symmetrical about the z axis, and Fig. 13 may be regarded as Fig. 12(*b*) multiplied by an appropriate factor and revolved about the z axis. Figures such as Fig. 13 do not express the " shape of the atom," since the values of OP from the three-dimensional diagram of Fig. 13 have to be multiplied by the radial probability factor in

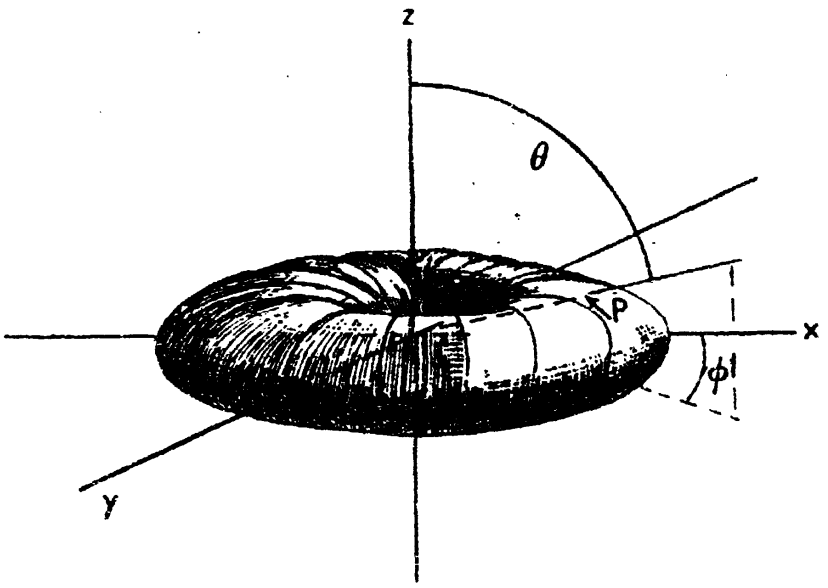


Fig. 13.

order to give the complete electron density. That is to say, the electron-cloud density at a given point is proportional to $OP \times R(r)R^*(r)$, at the point concerned, so that the values of OP for the different directions in Fig. 13 have to be multiplied by the value of $R(r)R^*(r)$ from a diagram such as that of Fig. 12(*a*) in order to indicate the total electron-cloud density. The electron-cloud pattern indicated by a combination of Figs. 12(*a*) and 13, would have a spherical node (*i.e.*, a zero electron density) of radius $r = a$, because the radial curve of Fig. 12(*a*) has a zero value at $r = a$. At other distances the electron-cloud density would be greatest in the xy plane, because the value of OP in Fig. 13 is greatest in this plane, and the electron-cloud density at all distances would be zero along the z axis, because, in Fig. 13, $OP = 0$ in this direction. The student must learn how to visualize the product of

the radial factor and the polar (directional) factors in order to appreciate the "shape" of the electron cloud, which is naturally often very complicated. If the radial factor indicates the presence of one or more spherical nodes, the inside of the atom will contain spherical shells on which the electron-cloud density is zero.

Generally speaking, however, the nodes of the radial probability factor concern the interior rather than the exterior of the atom, and at the outside of the atom the radial factor is diminishing continuously in a way similar to that shown in Fig. 12(*a*). When, therefore, we are dealing with the outside of the atom, diagrams such as those of Fig. 13 do give a general indication of the shape of the atom in the state concerned. At a given distance from the centre of the atom, the electron density is proportional to the lengths of *OP* in the different directions of Fig. 13, and hence the surfaces of constant electron density will project furthest in the directions for which *OP* in Fig. 13 has its greatest values, and the outside of the atom may be regarded as having the shape of Fig. 13 with the sharp bounding surface replaced by a diffuse electron cloud, the density of which diminishes as we proceed outwards.

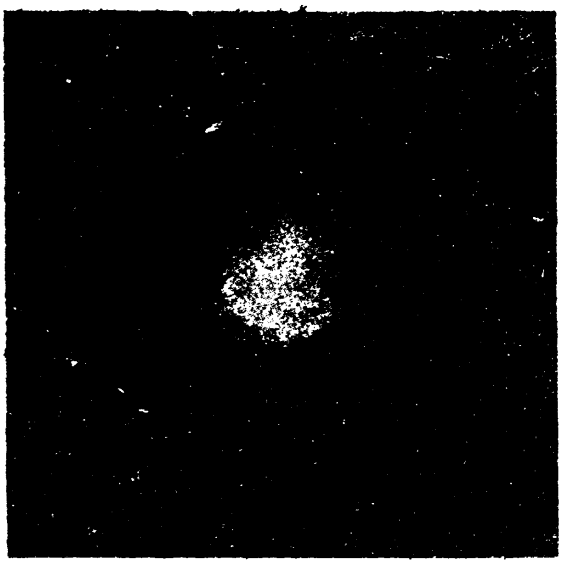
Chapter XII.—The *s*, *p*, and *d* States.

In the preceding chapter we have seen how the electron-cloud density in the space surrounding the nucleus of an atom is obtained as the product of the radial factor $R(r)R^*(r)$ at the distance concerned, and the length OP in the direction concerned in the 3-dimensional polar diagram, this diagram being a combination of the two 2-dimensional polar diagrams for the angles θ and ϕ. These polar diagrams indicate the variation of the electron-cloud density with direction, and were first calculated by means of the Schrödinger theory. This did not include the effects of electron spin, and the theory was later elaborated by Dirac to include the effects of spin. For the present purpose we shall concern ourselves almost exclusively with the Schrödinger diagrams, because in almost all cases of metallic and other combination, the perturbing forces are so much greater than the effects of spin that the Schrödinger theory is sufficient.

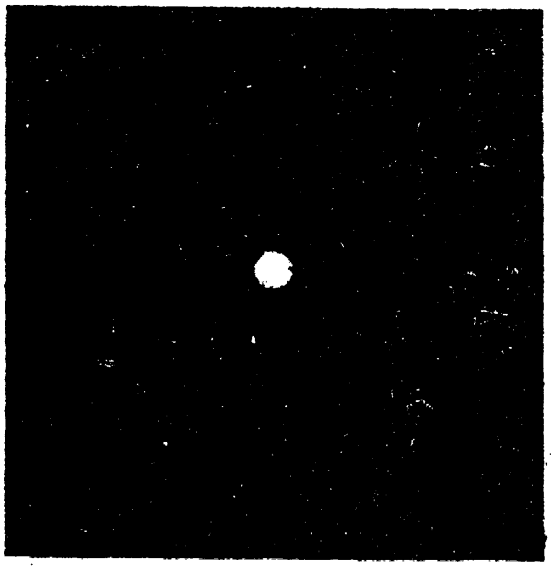
We may consider first the *s*-states, and for these the theories of both Schrödinger and Dirac require the electron clouds to be spherically symmetrical, and in the Schrödinger theory they are of such a nature that if n is the principal quantum number, the electron cloud has $(n-1)$ spherical nodes. The values of $\Theta(\theta)\Theta^*(\theta)$ and $\Phi(\phi)\Phi^*(\phi)$ are thus both constants, and the electron-cloud density can be represented by a single curve showing the variation of ρ, or of $U(r)$, as a function of the distance from the nucleus.

Fig. 14 shows the relation between ρ and r for the normal state, $(1s)^1$, of the hydrogen atom, and the corresponding relation between $U(r)$ and r. The picture of the atom represented by these curves is that of a nucleus surrounded by a spherically symmetrical ball of negative electricity, the density of which fades away rapidly at distances greater than about 2 A. Fig. 15(*a*) (Plate I) is an attempt to show this photographically by a method in which the brightness of illumination is proportional to the electron-cloud density.† This picture of an atom is clearly very different from that of the older theories of electrons in orbits, since these indicated an atom with the characteristics of a flat disc or ring. The older theories did, however, express part of the truth, for the radius of the first Bohr orbit of the hydrogen atom was 0·529 A., and as will be seen from Fig. 14, the $U(r)$ curve shows a maximum at this point, so that the electron may be said to spend more of

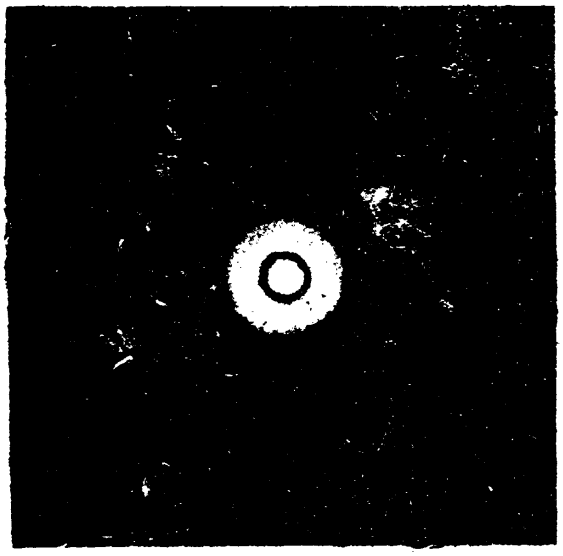
† The actual electron cloud is, of course, 3-dimensional



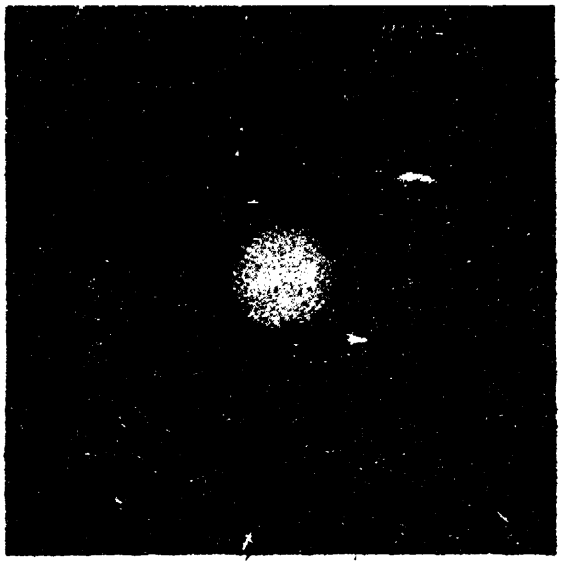
(*a*) Hydrogen $(1s)^1$ State.



(*b*) Hydrogen $(2s)^1$ State.



(*c*) Hydrogen $(3s)^1$ State.



[*Courtesy McGraw-Hill Publishing Company, Ltd.*

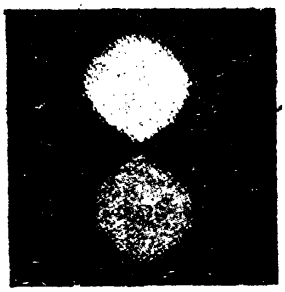
(*d*) Helium $(1s)^2$ State.

FIG. 15.—Distribution of the Function $\psi\psi^*$ for Certain States of Hydrogen and Helium.

Fig. 15(*a*) is an attempt to show the electron-cloud density of the hydrogen atom in the normal $(1s)^1$ state by a method in which the intensity of illumination is proportional to the electron-cloud density. Figs. 15(*b*) and (*c*) show the 2*s* and 3*s* states, and the scales on which these are shown are one-fifth and one-tenth of that of Fig. 15(*a*); from this it will be realized that the increase of the quantum number results in an enormously increased extent of the electron cloud. In the higher-quantum states, the electron cloud extends over a much larger region of space, but since the probability refers to one electron, the density must be very much smaller, and the intensities of Figs. 15(*b*) and (*c*) have therefore been increased by factors of 50 and 500 respectively, as compared with that of Fig. 15(*a*). If this had not been done, the outer rings of Figs. 15(*b*) and (*c*) would be too faint to be seen. Fig. 15(*d*) is a similar attempt to show the electron-cloud density of the helium atom in the normal $(1s)^2$ state. The scale of this is about the same as that of Fig. 15(*a*), but the intensity of the centre of Fig. 15(*d*) should be about 100 times as great as that at the centre of Fig. 15(*a*). The increased nuclear charge in helium has therefore drawn the electron cloud towards the nucleus, whilst the edge of the cloud is less diffuse.

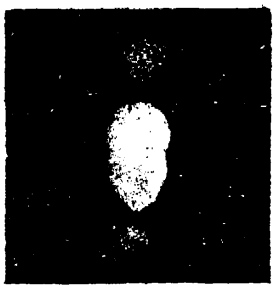
[*To face p.* 72.

PLATE II.



$2p$, $m = 0$.

FIG. 16.



[*Courtesy Physical Review.*

$3p$, $m = 0$.

FIG. 17.

FIGS. 16 and 17.—Photographs of the Electron Cloud for Various States of the Hydrogen-Like Atoms.

its time at a distance from the nucleus equal to that of the first Bohr orbit than at any other distance. In general, however, attempts to interpret electron-density figures in terms of orbits are dangerous, since an orbital model suitable for one purpose may not serve another.

Figs. 18(*a*) and (*b*) show the ρ and $U(r)$ curves for the hydrogen atom in the $(3s)^1$ state. Since $n = 3$, the pattern of the $(3s)^1$ state is characterized by $3 - 1 = 2$ spherical nodes, and the picture presented by the curves of these two figures is that of a spherically symmetrical ball of negative electricity surrounded by two spherical shells, the outer

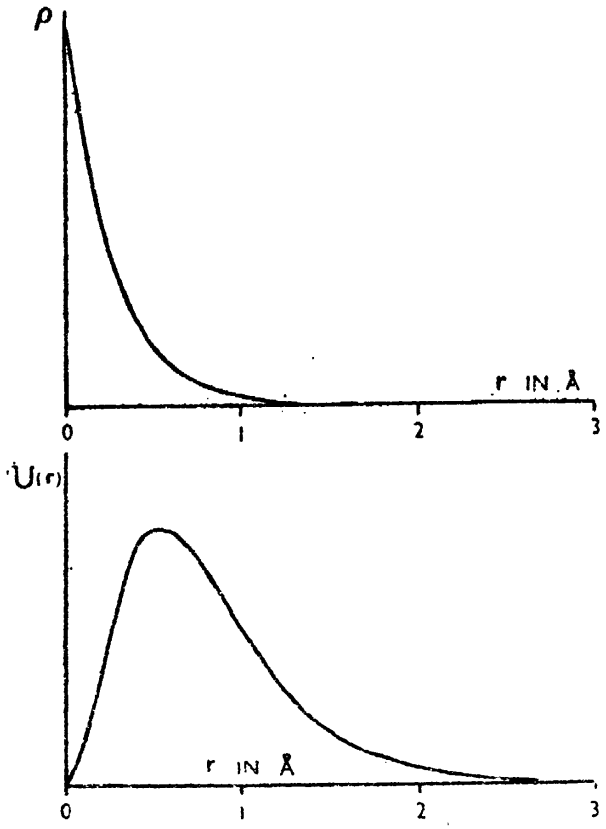


FIG. 14.—ρ and $U(r)$ Curves for Normal State of Hydrogen Atom.

of which is very diffuse. These diagrams show the danger of attempting to visualize the electron density from the $U(r)$ curve. In the $U(r)$ curve, the outermost maximum on the curve has the highest value of $U(r)$, although the value of the electron density ρ is comparatively small. This is merely the result of the fact that in a spherically symmetrical atom $U(r) = 4\pi r^2\rho$, and consequently ρ is multiplied by a term $(4\pi r^2)$ which becomes continually larger as we proceed outwards. Fig. 15(*c*) (Plate I) is an attempt to illustrate the electron-cloud pattern photographically by a method similar to that of Fig. 15(*a*), but this is really more like a cross-section through the spherically symmetrical pattern, and the pattern is, of course, 3-dimensional with

the nodes occupying spherical shells. The pattern for the $(3s)^1$ state occupies a larger region of space than that for the $(1s)^1$ state, showing that increasing quantum number produces a larger atom, just as in the older theories increasing quantum number resulted in a larger orbit. It must, however, be remembered that the whole pattern for

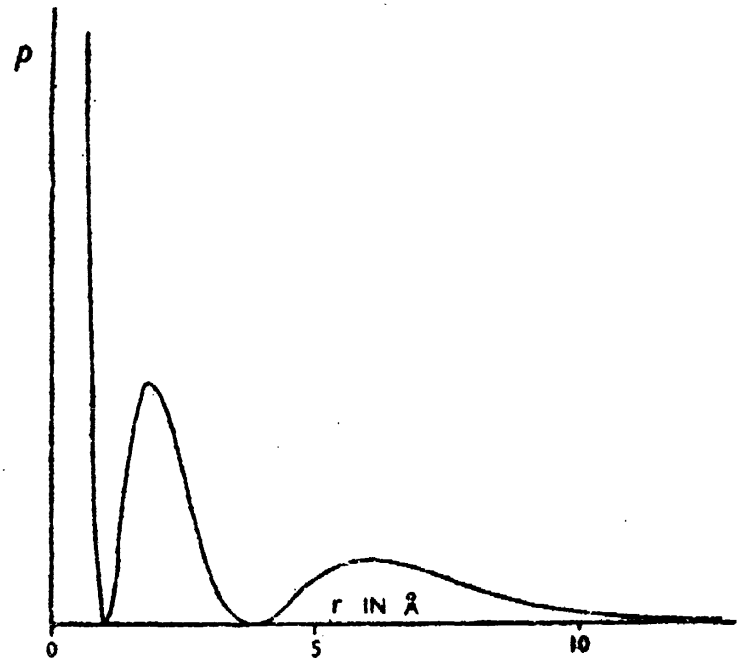


FIG. 18(*a*).

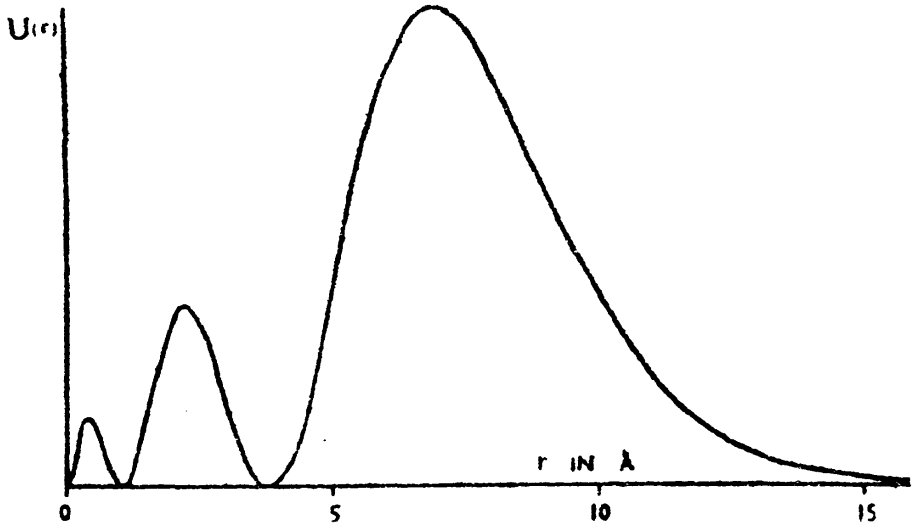


FIG. 18(*b*).

the $(3s)^1$ state still represents only one single electron, and consequently the electron density must on the whole be much less than in the pattern for the $(1s)^1$ state. As the description indicates, the scale of Fig. 15(*c*) is $\frac{1}{10}$th of that of Fig. 15(*a*), whilst the intensity of illumination of Fig. 15(*c*) has been multiplied by 500 in order to prevent the outermost parts of the pattern from being too faint to be seen. In the same way

the vertical scales in Figs. 18(*a*) and (*b*) have been greatly magnified as compared with the vertical scales in Fig. 14. Fig. 15(*b*) shows the corresponding patterns for the (2*s*) state of hydrogen atom, and this possesses $2 - 1 = 1$ spherical node; the scale and intensity of reproduction of Fig. 15(*b*) are intermediate between those of Figs. 15(*a*) and (*c*).

Electron-cloud patterns of the type shown in Fig. 18 have been objected to on the grounds that the existence of spherical nodes implies a definite probability of finding the electron in each region between the nodes, but no possibility of the electron travelling from one region to another. This criticism is, however, quite invalid, for as we have explained before (p. 48) the Indeterminancy Principle shows that it is meaningless to speak of the electron travelling about within an electron-cloud pattern representing an exact value of the energy. Since the energy is specified exactly, the time is completely indeterminate, and all that can be stated is the relative probability of finding the electron in different places in the space surrounding the atom.

For the radial part of the wave functions of the *s*-states, the curves of the Schrödinger and Dirac Theories are almost indistinguishable, except that the absolute spherical nodes of the Schrödinger theory are replaced by spherical shells in which the electron-cloud density, although very small, retains a finite value.

In atoms other than hydrogen, the symmetry characteristics of *s*-states are still retained, although the details of the radial probability curves are profoundly influenced by the different charges on the nuclei, and the screening effects of the different shells of electrons. An electron in an *s*-state always has a spherically symmetrical electron cloud with $(n - 1)$ spherical nodes, where n is the principal quantum number. It will help the description here if we anticipate later sections and explain that quantum groups of 8, 18, or 32 electrons also possess electron clouds with spherical symmetry. This means that atoms of the alkali metals, and also of copper, silver, and gold in their normal states, are spherically symmetrical,* since they may be regarded as consisting of the spherically symmetrical electron cloud of the valency electron of an *s*-state, superimposed on the spherically symmetrical atomic core with its groups of 8, 18, or 32 electrons. The alkaline earth atoms in their normal states are also spherically symmetrical, since both valency electrons are in *s*-states.

When we deal with electrons in metals, it frequently happens that an electron may be regarded as in a state derived from the *s*-state of

* For brevity we shall often refer to atoms or ions as being spherically symmetrical when we mean that their electron-cloud patterns have spherical symmetry.

the free atom. In such cases the electron-cloud pattern of an *s*-electron near to an ion has the same general characteristics as in the corresponding free atom, although the details are profoundly different at places where the electron is influenced to comparable degrees by two or more ions. Thus, in copper most of the valency electrons exist in states derived from the 4*s* state of the free atom, and the corresponding electron-cloud patterns *in the solid* have three nodes surrounding each ion. At distances very near to a nucleus, the $\rho(r)$ curves for the 4*s* electrons *in the solid* closely resemble those for the free atom, since here the electron is essentially under the influence of the one nucleus concerned. But at a point mid way between two ions in the solid, the electron is attracted equally in two directions, and the wave-function and $\rho(r)$ curves are quite different from those of the free atom.

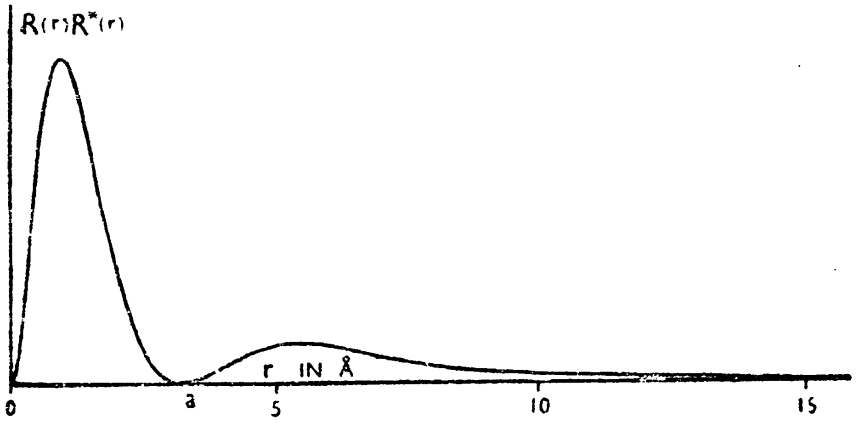


FIG. 19.

Similar considerations apply to electrons in states derived from the *p*- or *d*-states of free atoms.

We may next consider the electron-cloud pattern of the hydrogen atom in *p*-states, *i.e.*, for states in which $l = 1$. For each value of the principal quantum number n there are three *p*-states, corresponding with $m = 0$, and $m = \pm 1$, respectively. In the Schrödinger theory, the radial probability factor $R(r)R^*(r)$ for a *p*-state is different for each value of the principal quantum number n, but is the same for each of the three states ($m = 0$ and ± 1) of a given n. These radial probability factors are characterized by the existence of $(n - 2)$ spherical nodes, and also possess a node at the centre of the atom. Fig. 19, for example, shows the radial probability factor for the $(3p)^1$ state of the hydrogen atom, and the point *a* corresponds with a spherical node. The probability factor $\Theta(\theta)\Theta^*(\theta)$ involves the angle θ, and this involves the orientation of the atom. As explained before (p. 62), we cannot really speak of the orientation of a perfectly free atom, and the policy

adopted is to imagine that a magnetic field acts along the z axis, and that when the field is reduced to zero this axis persists, and that the same mathematical treatment is applicable. The theory then shows that the ϕ probability factor $[\Phi(\phi)\Phi^*(\phi)]$ is a constant, and that the electron clouds of the p-states are symmetrical about the z axis.

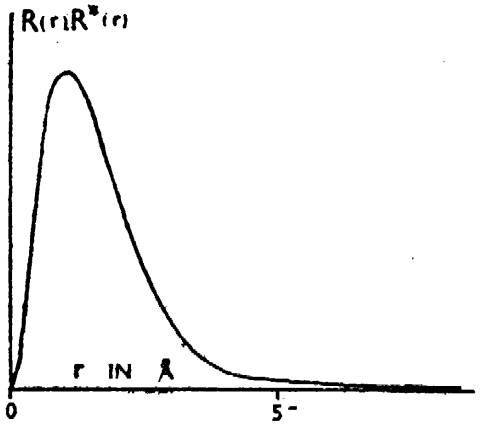
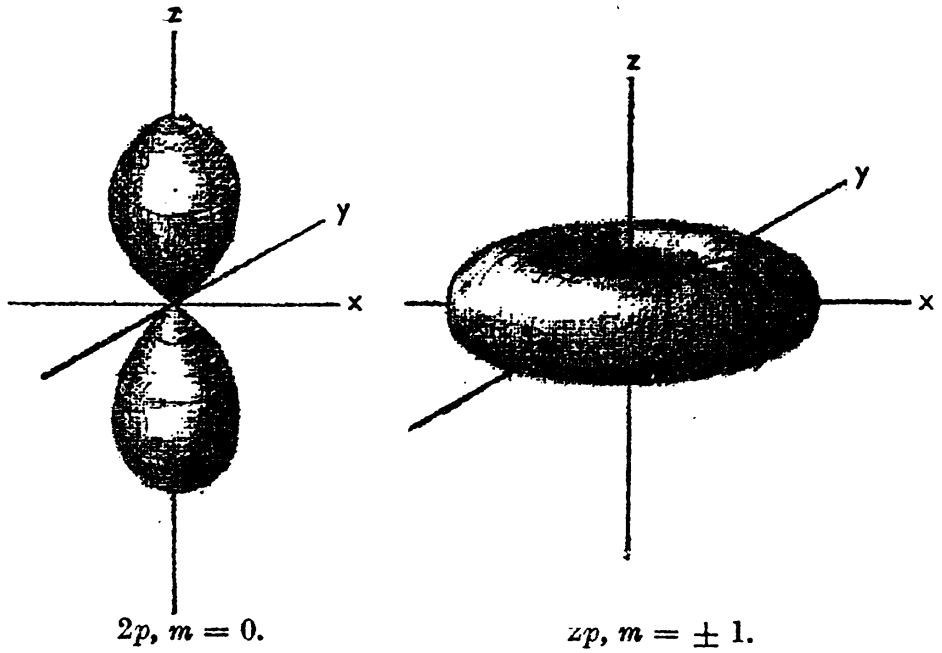


FIG. 20.

We may consider first the $2p$ state for which, since $n - 1 = 1$, there are no spherical nodes, and the radial probability factor is of the form shown in Fig. 20. There are then the three cases $m = 0$ and $m = \pm 1$, and the complete 3-dimensional polar diagrams are as shown in Fig. 21, and possess axial symmetry. The electron density at any point (r, θ, ϕ) is then obtained by multiplying the value of the radial probability factor at the distance r by the value of the polar factor for the direction concerned in Fig. 21. As previously explained, the outermost parts of the atom, where the radial probability curve is dying away gradually, may be regarded as having the "shape" of



$2p$, $m = 0$. $2p$, $m = \pm 1$.

FIG. 21.

Fig. 21, although the inner parts will be affected by the characteristics of the $(R(r)R^*(r))$ curve, and cannot be visualized simply. Fig. 16 (Plate II) is an attempt to show the $(2p, m = 0)$ state photographically, but this is more like a cross-section than a true 3-dimensional pattern.

When $n > 2$, the electron clouds of the p-states show $(n - 2)$ spherical nodes, and the radial probability factors analogous to Fig. 20 show $(n - 2)$ nodal points as well as the node at $r = 0$. The θ and ϕ probability factors are still given by the same polar diagrams of Fig. 21, and the electron cloud for, say, the $3p$ state may be looked on as more or less of the same nature as that of the $2p$ state, but with a spherical node inside the atom. Fig. 17 (Plate II) is an attempt to show this for the $(3p, m = 0)$ state, but the photograph is not very successful because the node at the centre is not clearly revealed. It must again be emphasized that the whole pattern represents only one electron.

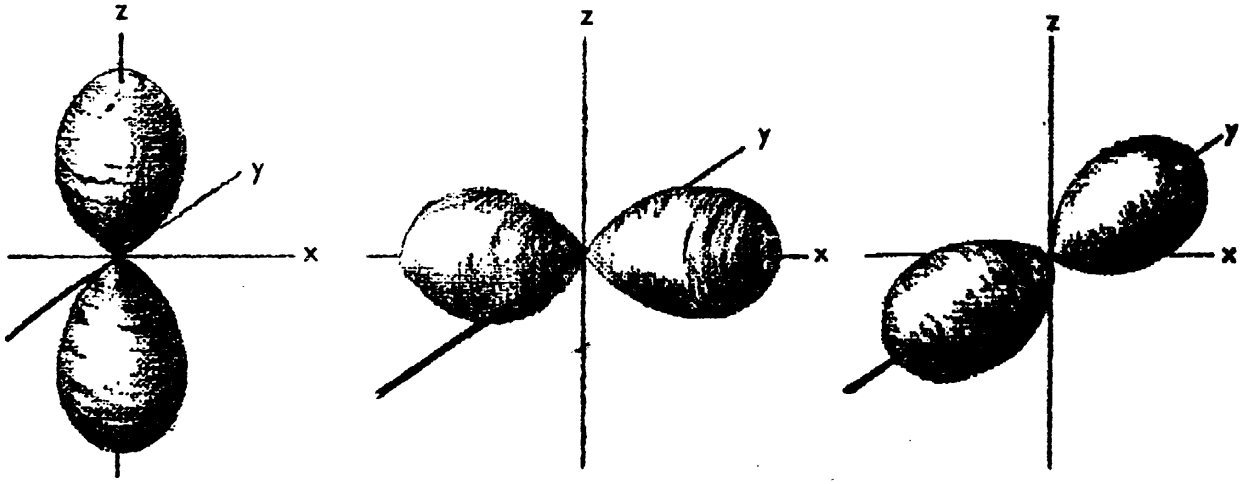
For free atoms, the electron-cloud pattern for the p-states with $m = +1$ and $m = -1$, are identical, and differ only in that the Φ functions are $e^{+i\phi}$ and $e^{-i\phi}$, respectively. These differ in the sense of rotation, *i.e.*, the direction of the angular momentum, but each is perfectly symmetrical about the z axis, and the picture presented is that in a weak magnetic field the orbital angular momentum vector precesses round the z axis, this precession being the cause of the axial symmetry of Fig. 21. Just as the z axis has to be defined with reference to something external to the atom (*e.g.*, the magnetic field), so the x and y axes can only be given a real physical meaning if the atom is submitted to the action of one or more additional fields, as, for example, by placing the atom in a crystal. Under these conditions, the two p-states with $m = +1$ and $m = -1$, respectively, have electron clouds which are perpendicular to one another in the xy plane, and the angular probability factors of the three p-states are of the form shown in Fig. 22, and are mutually perpendicular. This fact is of great importance in understanding the structures of some molecules and crystals.

It will be noted that in Fig. 21 the nodes of the one pattern are in the direction of the maximum value of the other, and the two combine to give an electron cloud of spherical symmetry. In the same way the three patterns of Fig. 22 add together to form a cloud of spherical symmetry. This means that an atom such as that of nitrogen, with one electron in each of the three p-states, is spherically symmetrical, whilst an $(ns)^2(np)^6$ group of electrons is also spherically symmetrical.

We shall not deal here with the Dirac theory of the p-states, since, as explained above, the differences between the Dirac and Schrödinger theories only concern the atom when the external fields are so weak that they are small compared with the effects of the electron spin. It should be noted, however, that the Dirac theory sometimes leads to a greater symmetry than the Schrödinger theory. Thus, in the Dirac theory one of the p-states is spherically symmetrical, and this applies not

only to the hydrogen atom, but also to atoms of boron, aluminium, gallium, indium, and thallium, and atoms of these elements are spherically symmetrical in the free state when the orientation is defined by a field weak compared to the spin effects.† In slightly stronger fields the Schrödinger theory is sufficient.

The preceding description of the *p*-states has shown how the electron-cloud density is obtained from the product of the radial probability factor $R(r)R^*(r)$, and the angular factors $\Theta(\theta)\Theta^*(\theta)$, $\Phi(\phi)\Phi^*(\phi)$, and we shall therefore only give a very brief description of the *d*-states. In the Schrödinger theory of the hydrogen atom, the radial probability factor of the *d*-states is characterized by a node at the centre of the atom, and by $(n - 3)$ spherical nodes.‡ The 3-dimen-



$m = 0$. $m = +1$. $m = -1$.

FIG. 22.

sional polar diagrams of the three states of the *d*-electron ($m = 0$, 1, 2) are shown in Fig. 23. For the free atom as defined by a weak magnetic field along the z axis, the electron clouds have axial symmetry.

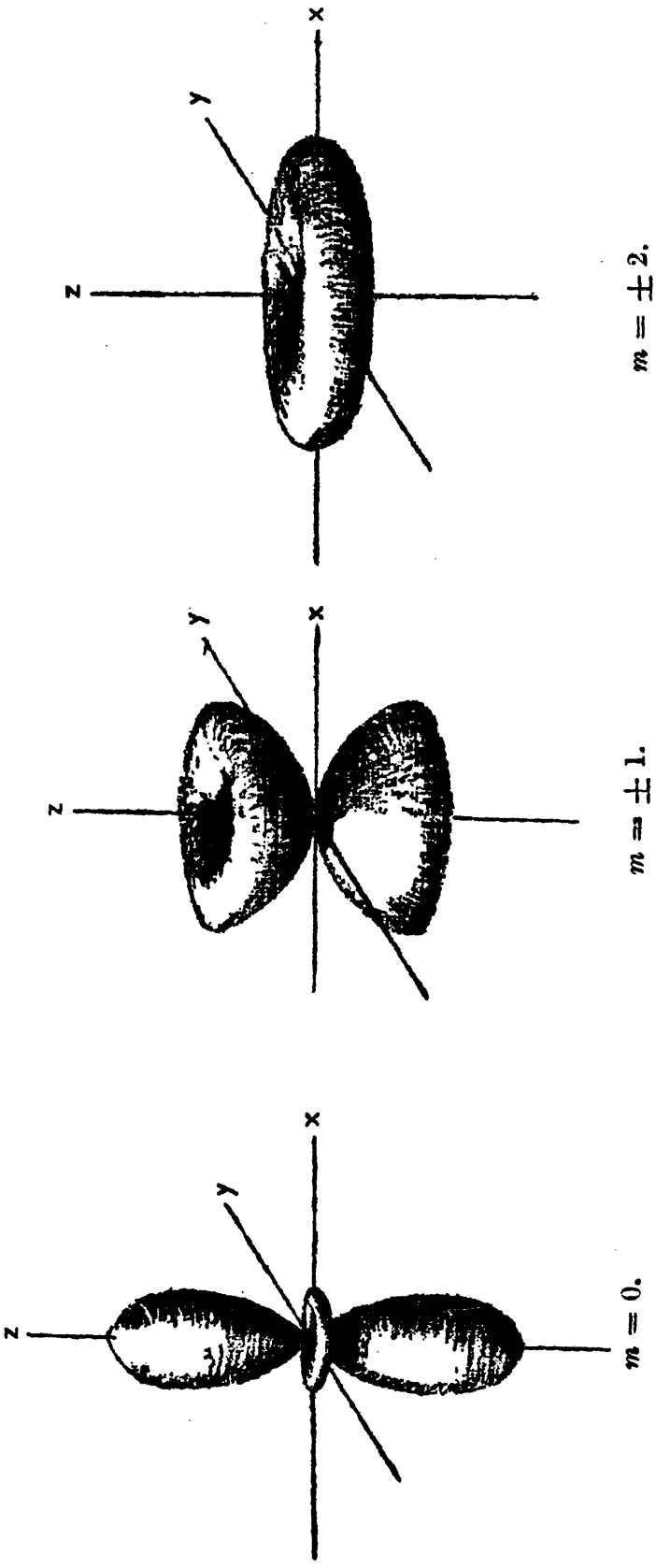
The state ($l = 2$, $m = 0$) is characterized by nodes at $\theta = 52°$ and $\theta = 128°$, and these nodes form the surfaces of two cones of half angle 52° about the z axis. The pattern has a maximum value for $\theta = 0$, *i.e.*, along the z axis, and there is a second but much smaller maximum in the xy plane.

The state ($l = 2$, $m = 1$) in the free atom is characterized by maxima at $\theta = 45°$ and $\theta = 135°$, and there is a node along the z axis, whilst the xy plane is a nodal plane. When the atom is in a crystal, or under some other restraint which gives the x and y axes physical

† For further details see White's "Introduction to Atomic Spectra," p. 142.

‡ It will be noted that the principal quantum number n has the meaning that $(n - l - 1)$ is the number of nodes of the radial probability factor excluding that at the centre of the atom.

significance, the two states $m = +1$ and $m = -1$ have electron clouds which are mutually perpendicular to one another, and the polar diagrams take the form shown in Fig. 24.

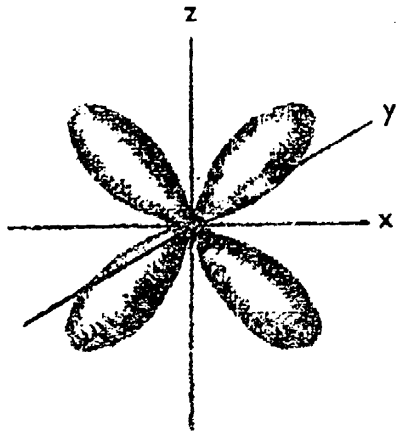


$m = \pm 2$. $m = \pm 1$. $m = 0$.

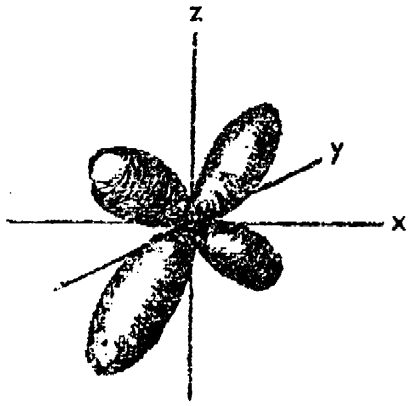
FIG. 23.

The state ($l = 2$, $m = \pm 2$) of the free atom is characterized by a node along the z axis, and the electron density is greatest in the xy plane. When the atom is in a crystal or under some other restraint which gives the x and y axes a physical meaning, the electron clouds of the two states are mutually inclined at 45°, as shown in Fig. 24.

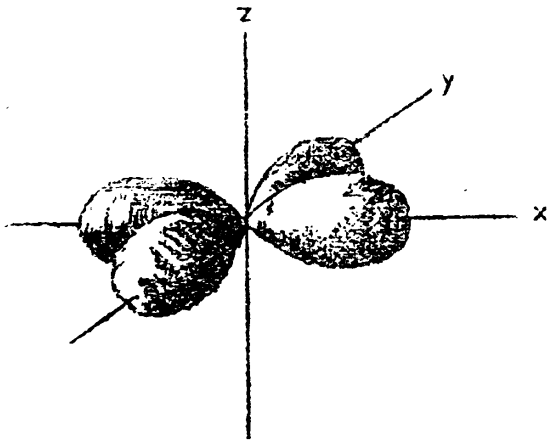
The complete set of d-patterns when superimposed on one another gives a pattern of spherical symmetry, so that a group of 10 d-electrons



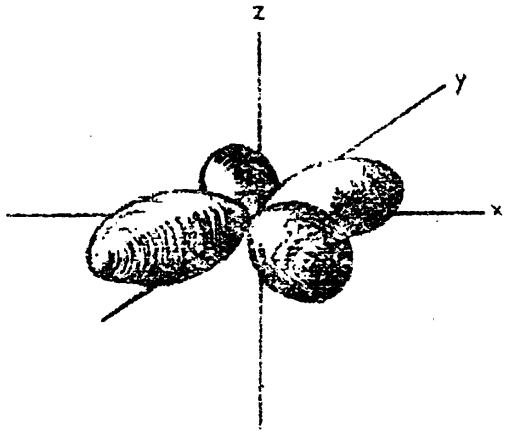
$l = 2$, $m = 1$. Maxima at $\theta = 45°, 135°$, $\phi = 0°, 180°$.



$l = 2$, $m = -1$. Maxima at $\theta = 45°, 135°$, $\phi = 90°, 270°$.



$l = 2$, $m = 2$. Maxima along x and y axes.



$l = 2$, $m = -2$. Maxima at 45° to x and y axes.

FIG. 24.

is spherically symmetrical, and a group of 18 electrons is also spherically symmetrical, since it is composed of the superimposed patterns of the spherically symmetrical $(ns)^2(np)^6$ and $(nd)^{10}$ sub-groups.

It will be noted that in the p- and the d-states, increasing value of the quantum number m_l results in the electron cloud becoming more and more concentrated in the xy plane, and this is a general principle for the higher (f, g, . . .) states.

PART III.—ASSEMBLIES OF ATOMS.

Introduction.

In Part II we have described the structures of free atoms, and how these are interpreted in terms of the new theories. We have now to consider the nature of the interatomic forces involved in the formation of solids, liquids, and compound molecules. It will be appreciated that the problem of the cohesive forces in solids and liquids is only part of the general problem of interatomic cohesion, and, as we shall see later, there are some solids in which the forces between the atoms are of exactly the same nature as those involved in the formation of compound molecules. In many senses a crystal of a metal is to be looked on as an immense molecule of the atoms concerned, and in order to understand the structure we need first of all to determine the type of crystal structure and then the energy characteristics of the electrons in the solid. The determination of the crystal structure is carried out by means of X-ray diffraction methods, and in the present book we shall accept the results of this work and not concern ourselves with the experimental methods. Just as the energy characteristics of molecules are deduced from the analysis of molecular spectra, so the energies of electrons in solids can be studied by the analysis of the X-ray spectra of solids. Historically, this is a comparatively new branch of science, but it is of such fundamental importance that we shall consider it in the next chapter. We shall then review, in Chapter XIV, some of the characteristics of the elements, and show that the latter fall into four main classes, in which distinct types of interatomic forces can be recognized as responsible for the formation of either molecules or crystals; these can be considered as assemblies of like atoms. In Chapter XV we shall consider what happens in mixtures or compounds of unlike atoms, and shall see that in many cases the interatomic forces are clearly of the same nature as those found in the molecules or crystals of the elements, but that a new type of force, the *ionic bond*, is also met with, and we shall show how this kind of force exerts an influence in many alloy structures. In Chapters XVI–XIX we shall consider in greater detail the electronic processes involved in three of the other main types of interatomic attraction, namely the van der Waals or Polarization Forces, the Exchange Forces, and the Wave-Mechanical Resonance Forces. The metallurgical student should appreciate that, although much of the description refers to non-metallic substances, the processes described are often present in solid metals and alloys, even though they are confused by the simultaneous presence of other types of interatomic attraction.

Chapter XIII.—The Soft X-Ray Spectra of Solids.

In Part II we have seen how the electrons in a free atom occupy a series of energy states, each characterized by the appropriate values of the four quantum numbers n, l, m_l, and m_s. In the normal state of a free atom, the electrons are divided among the different quantum states in such a way as to give the lowest possible energy, subject to the Pauli restriction principle that not more than one electron occupies a state as defined by a given combination of all four quantum numbers. It is these electronic configurations or groupings which are given in Table II, and these groupings give the electronic structures of the free atoms in their normal states. Under appropriate conditions, such as the high temperatures of flames or electric discharges, a free atom can undergo electronic excitation into a state of higher energy. Thus the normal state of the sodium atom is $(1s)^2(2s)^2(2p)^6(3s)^1$, but under appropriate conditions the valency electron can be excited into a state of higher energy, so that an excited atom with a configuration such as $(1s)^2(2s)^2(2p)^5(3p)^1$ is formed, and this has a higher energy than the normal state, because the $(3p)$ state is higher than the $(3s)$ state. If the electron then falls back from the excited state to the normal state, the atom emits radiation of frequency ν, given by the relation :

$$E_1 - E_2 = h\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{III (1)}$$

where E_1 and E_2 are the energies of the excited and normal states respectively. In the case described above the excitation affects the valency electron only, but this is not necessarily so, and an excited state such as $(1s)^2(2s)^2(2p)^5(3s)^2$ might be formed, and this would then revert to the normal state by one of the $(3s)$ electrons dropping back into the $(2p)$ sub-group. Speaking generally it may be said that the ordinary optical spectra correspond to transitions between electron states in the one or two outermost quantum shells of a free atom. Since visible light has wave-lengths of the order of 5000 A. and the velocity of light is of the order of 3×10^{10} cm./sec., the frequencies of the optical spectra are of the order 6×10^{14}, and since $h = 6{\cdot}5 \times 10^{-27}$ g.cm.^{2} sec.$^{-1}$, the transitions involved concern energy differences of the order of 10^{-12} erg/atom.

Under appropriate conditions it is possible to excite the electrons in the lower energy states of a free atom. Thus the free atom of sodium might be excited into a state such as $(1s)^1(2s)^2(2p)^6(3s)^1(3p)^1$ in which one of the $(1s)$ electrons has been excited into a $(3p)$ state. In this case if the $(3p)$ electron drops back into the $(1s)$ level, the energy change

involved is of the order of 10^{-9} erg/atom, and is thus very much greater than those taking place in the optical spectra referred to above. This kind of transition involving the inner levels of an atom gives rise to X-ray spectra, in which the wave-lengths are of the order of 1 A. unit. It is customary to use the symbols K, L, M . . . to denote the groups of electrons with principal quantum numbers $n = 1, 2, 3$ . . . and the K X-ray emission spectra are those in which the excitation expels an electron from the K shell, and emission occurs when an electron falls back from one of the outer shells. Thus, in the case of aluminium, the electronic structure of the normal state of the free atom is :

$$\underbrace{(1s)^2}_{K}\ \underbrace{(2s)^2(2p)^6}_{L}\ \underbrace{(3s)^2(3p)^1}_{M}$$

and if an electron is expelled from the $(1s)$ or K-shell, the $K\alpha$ emission spectra are the result of an electron falling back from the L shell to the K shell, whilst the $K\beta$ emission spectra result from an electron falling from the M shell to the K shell. Since the energy difference between the K and M shells is greater than that between the K and L shells, it follows from equation (1) that the $K\beta$ emission line has a higher frequency, *i.e.*, is harder, than the $K\alpha$ emission line.

A free atom can thus exist in a number of energy states, each characterized by a definite energy and by a definite distribution of the electrons among the possible quantum states. The lines of the optical or X-ray spectra of free atoms are due to transitions of the atom from one state to another, and the sharpness of these lines is the result of a definite energy being associated with each state. It is not, however, possible for transitions to occur between any two electron states of an atom, and the possible transitions are controlled by what are known as *Selection Rules*. Of these the most important is that the probability of a transition occurring is very small unless the quantum number l changes by 1. Thus transitions can occur from a p-state to an s-state, or from a d-state to a p-state, but not between two s-states. There is no restriction on the change of the principal quantum number n. In the case of K X-ray emission spectra, for example, the electron jumps into the $(1s)$ state from a state in an outer quantum shell. Here the final state after the transition is $(1s)$, for which $l = 0$, and so we do not obtain an X-ray line corresponding to a transition from a $(2s)$ state to a $(1s)$ state, but we do obtain transitions from a $(2p)$ state to a $(1s)$ state, since here l changes by 1; the resulting X-ray line is called the $K\alpha$ emission line, and is a doublet (*i.e.*, two lines of nearly the same wave-length) because the $(2p)$ sub-group of the free atom is divided into the sub-sub-groups which have very slightly different energies.

In the L X-ray spectra, an electron is excited from the L shell, and emission results from one of the outer electrons jumping into the unoccupied state. In this case the possibilities are more numerous, since the L or 2-quantum shell contains both $2s$ and $2p$ electrons. If one of the $2s$ electrons is excited, the selection rule indicates that X-ray spectra may result from an electron falling back from $3p$, $4p$, &c., subgroups. If, on the other hand, one of the $2p$ electrons is excited, X-ray lines are not found for transitions from a $(3p)$ to a $(2p)$ state, since for this l would change by 0, but X-ray lines are found for transitions from $(3s)$, $(3d)$, $(4s)$, or $(4d)$ states to the $(2p)$ state, since the transitions $s \rightarrow p$ or $d \rightarrow p$ mean that l changes by 1. There is thus a whole group of L-emission lines corresponding to the different possible transitions.

The above remarks refer to free atoms, and it is by the study of the frequencies and intensities of the emission lines that the spectroscopist has been able to deduce the energies of the different electronic states of atoms and the probabilities of transitions occurring from one state to another. When we deal with crystals, we are concerned with immense assemblies of atoms at distances of the order of 10^{-7} to 10^{-8} cm. from one another. The conditions are thus very different from those of free atoms, but speaking generally, the wave functions of an electron in the periodic field of a crystal may be regarded as derived from the wave functions in the free atom, and retain some of the symmetry characteristics of the $s, p, \ldots$ states. In the case of sodium, for example, the valency electrons of the free atoms are in $(3s)$ states, and in crystals of sodium there are electrons in states derived from the $(3s)$ states of the free atom, and possessing $n - 1 = 3 - 1 = 2$ nodes round the centre of each atom. In this case the innermost two nodes will be approximately spherical, but the outermost node will be distorted, although the total number of nodes will remain at three per atom. In the same way the $(1s)$, $(2s)$, and $(2p)$ states of the free atom give rise to corresponding electronic states in the solid. Just as the energy characteristics of the electrons in a free atom can be determined from a study of the emission spectra of free atoms which have been excited in an electric discharge, so the energies of electrons in a crystal can be deduced by investigating the spectra emitted by solids in which excitation has been produced by suitable means, the most usual method being by electron bombardment. The experimental methods are naturally complicated, but the underlying principles are very simple. When a metal such as aluminium is bombarded by electrons, the atoms receive an intense stimulus, as a result of which an electron may be expelled from one of the lower electron shells, say the K or $(1s)$ shell. An electron may then fall back

from the L shell to the K shell, with the production of a quantum of radiation of frequency given by equation III (1). The frequencies of this emission, the $K\alpha$ emission, then indicate the differences in energies of the K and L electrons *in the solid crystal*, as distinct from their differences in the free atom. Alternatively, an electron might fall back from the $(3p)$ state to the $(1s)$ state, and the resulting $K\beta$ emission would indicate the differences between the energies of the $(3p)$ and $(1s)$ electrons in the solid. The selection principles referred to above still apply, and the K emission spectra of the solid could not be used to deduce the characteristics of the $(3s)$ electrons in aluminium, since a $(3s) \rightarrow (1s)$ transition is prohibited. For this purpose the spectral region corresponding to the L_3 emission would be studied, since this emission corresponds to the transition $(3s) \rightarrow (2p)$. In this way, by choosing the appropriate X-ray emission spectra, the physicist is beginning to explore the energy characteristics of electrons in solid crystals, just as the earlier spectroscopy investigated the energy characteristics of free atoms. Very beautiful work on the soft X-ray spectroscopy of the solid state has been carried out by H. W. B. Skinner; by using targets cooled by liquid air it has been possible to examine the effect of temperature on the energies of electrons in a metal. The experimental details of this work lie outside the present book, but the main conclusions of this and other work will be summarized briefly.

By a free atom, we mean in practice an atom in a very dilute gas, and if we imagine an immense assembly of free atoms to be gradually compressed to form a dense gas, or a liquid, or a solid, the general effect is for each sharp energy level of the free atom to be broadened into a band or range of energy levels. The details of the process depend on the electron state and the atom concerned, and on the structure of the solid or liquid which is formed, but the broadening of the sharp levels of a free atom is a quite general process.

For the lowest electron states of all but the lightest elements, the broadening of the energy level is negligible at the interatomic distances with which we are concerned in solids and liquids. It is for this reason that we still obtain sharp $K\alpha$ emission *lines* from solid elements such as copper, since these correspond with transitions between the K and L shells, which in the heavier elements are too deep down in the atom to be affected appreciably by the influence of other atoms at distances of the order of 10^{-8} cm. For the same reason these emission lines are practically independent of the state of combination of the copper atom, because although the chemical combination affects the outer electrons profoundly, the inner electrons are so predominantly under the influence of the one nucleus that they are practically undisturbed by changes in

the electron distribution at the outside of the atom. It is for this reason that in X-ray crystal analysis the wave-length of the copper $K\alpha$ radiation is unaffected by superficial oxidation or contamination of the copper target.

When the assembly of free atoms is gradually compressed, the broadening of the energy levels of the outermost electrons eventually becomes appreciable, and at interatomic distances of the order of 10^{-7} to 10^{-8} cm. each energy level of the valency electrons has broadened into a wide band of allowed energies. In its simplest form this may be represented by a diagram of the type shown in Fig. 25, in which the widths of the energy levels are plotted against $1/r$, where r is the distance of between two atoms in the assembly. The dotted line indicates an interatomic distance of the order 3×10^{-8} cm. at which the broaden-

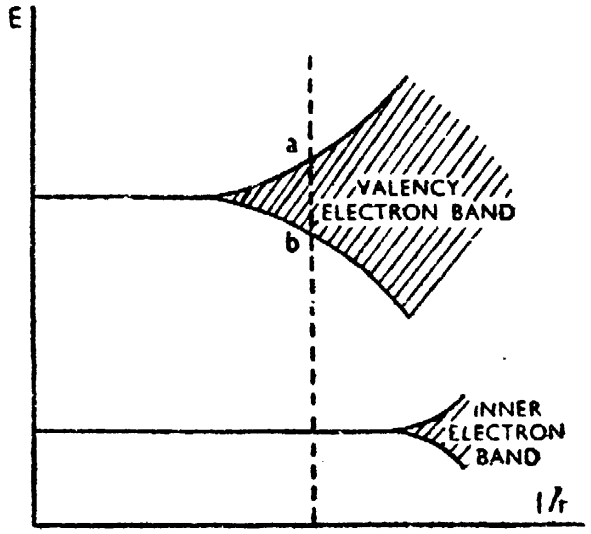


FIG. 25.

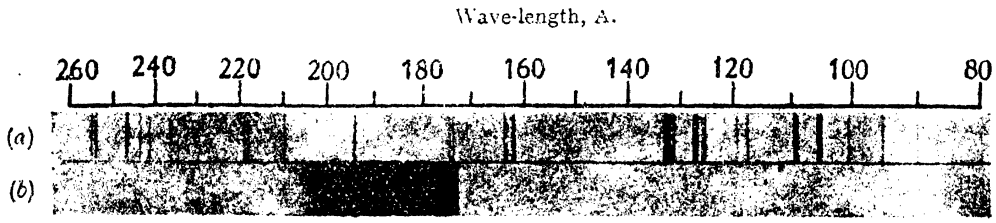
ing of the valency electron level is appreciable, whilst the inner electron level is practically unaffected.

From a figure of the above type it will be appreciated that if we consider radiation caused by the transition of an electron from the valency electron level to the K shell, then at interatomic distances of the order of 10^{-8} cm. there is no longer one constant difference in energy between the states before and after the transition. When the interatomic distances are of the order of 10^{-8} cm., the energies of the valency electrons of the assembly extend over a range, and consequently, according to equation III (1), there will be a range of possible frequencies, and the emission will consist of an emission *band*, instead of a single sharp line. In actual practice this is what occurs, and Fig. 26 (Plate III), which is due to Skinner, shows the sharp X-ray *line* spectrum of the free atoms of aluminium compared with the X-ray band spectrum obtained from

solid aluminium. Since it is known that the innermost electron levels are unaffected by the compression of atoms to interatomic distances of the order of 10^{-8} cm., the above type of X-ray emission spectrum shows conclusively that the sharp energy levels of the valency electrons have broadened into a band or range of possible energy states, and for solid metals the width of the valency electrons band is of the order 1–10 e.v. The study of the energy distribution in these emission bands enables us to deduce the energy characteristics of the valency electrons in the solid metal.

Fig. 25 shows clearly that as the assembly of atoms is compressed more and more closely, the valency electron band becomes wider, and speaking generally it may be said that in an assembly of atoms, the width of the band depends essentially on the mean interatomic distance, whilst the number of energy states within the band increases with the number of atoms in the assembly, and hence with the size of the crystal if we are dealing with a solid metal. We may suppose, for example, that in Fig. 25 *ab* represents the width of the band at the actual interatomic distance of a particular metal. If we then compare a large crystal with a small crystal, the width of the band *ab* will be the same in both cases, but the number of individual energy states in the range *ab* will be the greater for the larger crystal.

The ideas expressed in Fig. 25 lead at once to a further and most important conclusion. We may suppose that Fig. 27(*a*) shows diagrammatically the energy levels of the free atom of sodium. Then in the free atom of sodium the electrons will occupy the $(1s)^2(2s)^2(2p)^6(3s)^1$ levels, and there will be one electron in the $3s$ state and none in the $3p$ state (see Table II). Fig. 27(*b*) shows diagrammatically how the energy levels broaden when an assembly of sodium atoms are brought together, and the line *xy* indicates the interatomic distance in the crystal of sodium. At this distance the broadening of the $(1s)$, $(2s)$, and $(2p)$ levels is negligible, but the $(3s)$ and $(3p)$ levels have broadened to such an extent that they overlap. When this stage is reached, a process known as " hybridization " occurs, and the valency electrons exist, not in $(3s)$ or $(3p)$ states, but in a condition which may be described by the superposition of the two wave functions. Such electrons are said to exist in *hybrid orbitals*, and in sodium, for example, the valency electrons exist in $(3s)(3p)$ hybrid orbitals. In this case the work of Skinner shows that the valency electrons of lowest energy are in a condition closely resembling that of $(3s)$ electrons as modified by the crystal lattice, and that with increasing energy the $(3p)$ characteristics become more and more pronounced. Strictly speaking, we should not describe such electrons as existing in s or p states, but should



[*Courtesy Physical Society.*

FIG. 26.—Emission Spectra of Aluminium, (*a*) from vapour and (*b*) from solid.

PLATE III.

[*To face p.* 88.

always think of the hybridized condition. It is, however, common practice to refer to electrons in metals as belonging to *s*-bands, *d*-bands, &c., and for many purposes this is permissible provided that the true state of affairs is borne in mind. Thus the work of Skinner shows that solid sodium gives rise to a $K\beta$-emission spectrum, and this is commonly referred to as corresponding with an electronic transition from a $(3p)$ state to a $(1s)$ state. Strictly speaking, we should say that the $K\beta$ spectrum reveals the $3p$ fraction of the $(3s)(3p)$ hybrid, but as an ap-

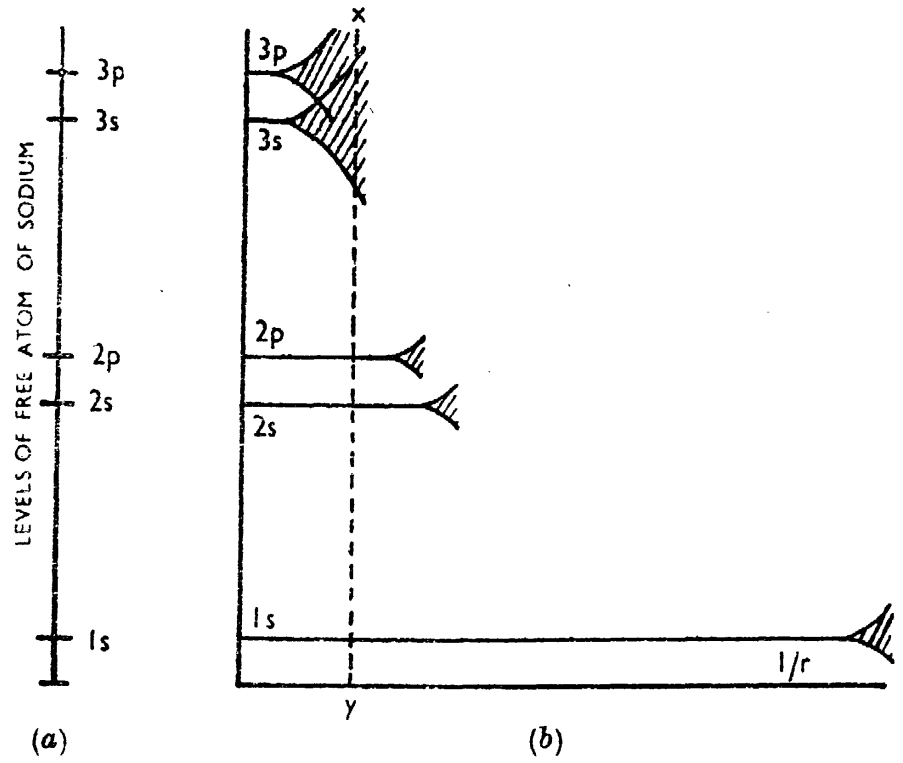


FIG. 27.

Fig. 27(*a*) shows diagrammatically the energy levels of the free atom of sodium. The vertical scale is purely diagrammatic and does not represent accurately the relative distances between the different energy levels. An accurate drawing would require the 1*s* level to be very much lower, and the difference between the 3*s* and 3*p* levels to be very much less than that shown.

Fig. 27(*b*) shows diagrammatically how the levels broaden as the atoms are brought together. The dotted line corresponds to the interatomic distance in the crystal of the metal.

proximation we may say that a fraction of the valency electrons are in $(3p)$ states, and similarly in other cases.

The above considerations will indicate how important it is to realize that the electronic configurations of Table II are the electronic structures of *free atoms*, and that the details of the distribution of the outer electrons are often quite different in a solid or liquid metal. Even in a simple univalent metal, such as sodium, the solid metal contains its valency electrons in $(3s)(3p)$ hybrid orbitals, and some $(3p)$ character-

istics are developed, whilst in the divalent element magnesium the valency electrons are also in $(3s)(3p)$ hybrids, and for the electrons of higher energy the $(3p)$ characteristics are predominant, although in free atoms of magnesium, the two valency electrons occupy the complete $(3s)^2$ sub-group, and there are no electrons in $(3p)$ states. Here we may say that a considerable proportion of the valency electrons in solid magnesium exist in $(3p)$ states, although the true condition is one of hybridization. In the same way in the transition elements the relative numbers of electrons in the $(n\text{-}1)d$ and ns states may be quite different in the free atoms and the solid metals. Thus the free atom of nickel has the configuration $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^8(4s)^2$, but in solid nickel there are on the average only 0·6 electrons per atom in $(4s)$ states, and 9·4 electrons per atom in $(3d)$ states. In some metallurgical papers there has been an unfortunate tendency to ignore these differences, and quite misleading conclusions have been drawn by assuming that the details of Table II apply to the outer electrons of solid or liquid metals. It will be appreciated that when we deal with the inner electrons of an atom, the electronic distributions in the solid metal and the free atoms are identical. In the case of nickel, for example, the free atoms and the solid metal have the same electron distribution as regards the $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$ groups.

It will be seen, therefore, that the experimental work on the soft X-ray spectroscopy of solids leads to the direct conclusion that the energies of the valency electrons of a metal are distributed over a band or range of energies, in contrast to the sharp energy levels in free atoms. By measurements of the variation of intensity across an emission band, it is possible to deduce the distribution of the electrons among the various possible energy states of the valency band, *i.e.* across the range of energies ab in Fig. 25. To describe these results, it is necessary to have some method of expressing the energy distribution, and this is done by means of what is called an $N(E)$ curve. For this purpose we may first define $n(E)dE$ as the number of electrons per unit volume of metal with energies between E and $E + dE$, and it is customary to plot $n(E)$ against E. In Fig. 28(a), for example, the curve indicates that the electrons have energies extending over the range a–b, and that the number of electrons with energies in the neighbourhood of a particular value E increases continuously with increasing E, until the energy reaches the value b, beyond which $n(E) = 0$, indicating that no electrons have energies greater than $E = b$. In this case the high-energy end of the band would be sharp. Fig. 28(b) would indicate that the electronic energy distribution for the valency electrons of low energy was the same as that of Fig. 28(a). The steep fall in the $n(E)$ curve at x indicates

that the number of electrons with energies beyond this point becomes very small and gradually vanishes, but there is no sharp upper limit to the energies of the electrons, and the head of the emission band would be diffuse. The curves in Fig. 28(*c*) would indicate that the valency electrons had energies extending over the ranges *a*–*b*, and *c*–*d*, but that no electrons had energies in the range *b*–*c*. These $n(E)$ curves are therefore nothing more than ways of showing how the electrons are distributed over the ranges of energy concerned.

The probability of a transition occurring from one electron state to

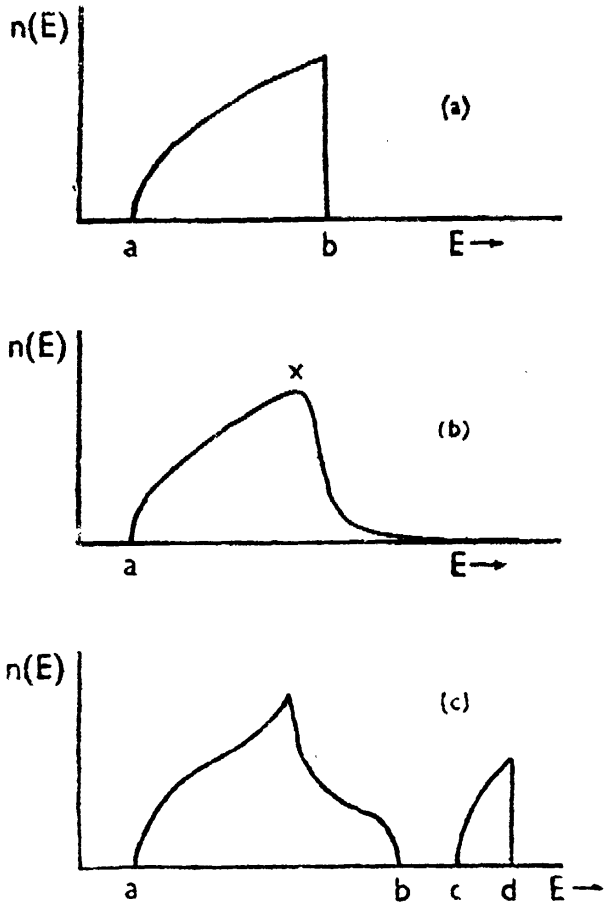
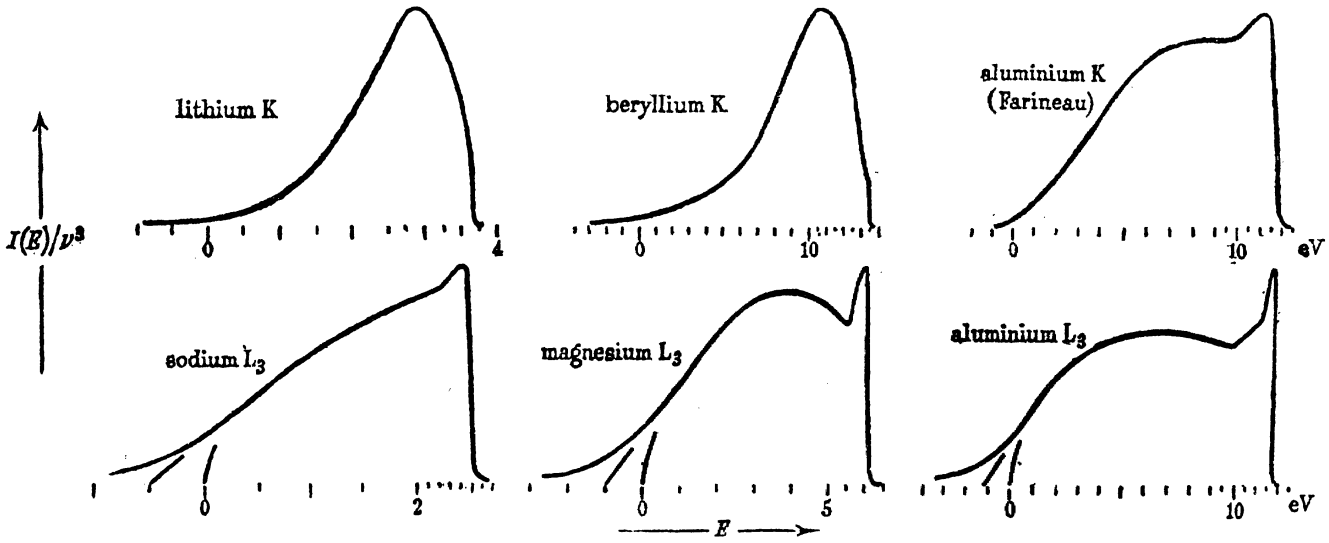


FIG. 28.

another is proportional, among other things, to the number of electrons present in the first state, and hence it will be readily understood that the $n(E)$ curves are of roughly the same form as the curves which show the variation of intensity over the emission bands of the soft X-ray spectra concerned. Actually the interpretation is not quite so simple, but these complications lie outside the scope of the present book,* and for the present we shall assume that the intensity curves are a direct indication

* The reader may consult H. W. B. Skinner, *Phil. Trans. Roy. Soc.*, 1940, [A], **239**, (801), 95.



[*Courtesy Royal Society.*

FIG. 29.—*K* and *L* Bands of Metals.

of the $n(E)$ curves. Fig. 29 is due to Skinner,* and shows the L_3 emission band for sodium; since the L_3 emission corresponds to a transition from the $(3s)$ band to the $(2p)$ state,† this curve gives the form of the $n(E)$ curve for the valency electrons of solid sodium existing in $(3s)$ states in the solid.‡ Fig. 29 also shows the K emission band for lithium, and since this corresponds to transitions from the $(2p)$ to the $(1s)$ state, the curve gives the form of the $n(E)$ curve for the $(2p)$ electrons in solid lithium; a curve of more or less the same shape would give the $n(E)$ curve for the $(3p)$ electrons in solid sodium.

As can be seen from Fig. 29, the corresponding K and L_3 curves for magnesium and aluminium are clearly more complicated in form at the high-energy end. Fig. 30 shows the effect of temperature on the high-energy end of the emission band, and from this it will be seen that the curve falls more steeply as the temperature is lowered.

It must be emphasized that the above curves are purely experimental. They lead directly to the conclusion that the energies of the valency electrons in metals extend over a range, and that the high-energy end of the range terminates more and more abruptly as the temperature becomes lower. At the absolute zero the $n(E)$ curve would terminate sharply with a vertical line at the high-energy end. At other temperatures, as shown in Fig. 30, the end of the band becomes diffuse, and the width of this temperature broadening is of the order $k\theta$, where θ is the absolute temperature; so that at room temperatures the diffuse head of the band extends over about $\frac{1}{10}$th e.v., as compared with a total band width of the order of 5–10 e.v. The curves also make it clear that with increasing valency, the characteristics of the energy distribution become more complicated. All this is now definitely established fact, and has to be explained by any satisfactory theory of metals. We may here anticipate some of the later theory and explain that a metal crystal is to be regarded as containing an immense number of possible electron states, and that at the absolute zero of temperature the N valency electrons of a crystal occupy the $N/2$ lowest energy states of the valency electron band, each state containing two electrons, one of each spin. At the absolute zero of temperature all the energy states up to a particular limit are occupied, and all those above this limit are unoccupied. The electronic-energy distribution curve thus shows a sharp limit; and it is this which corresponds with the

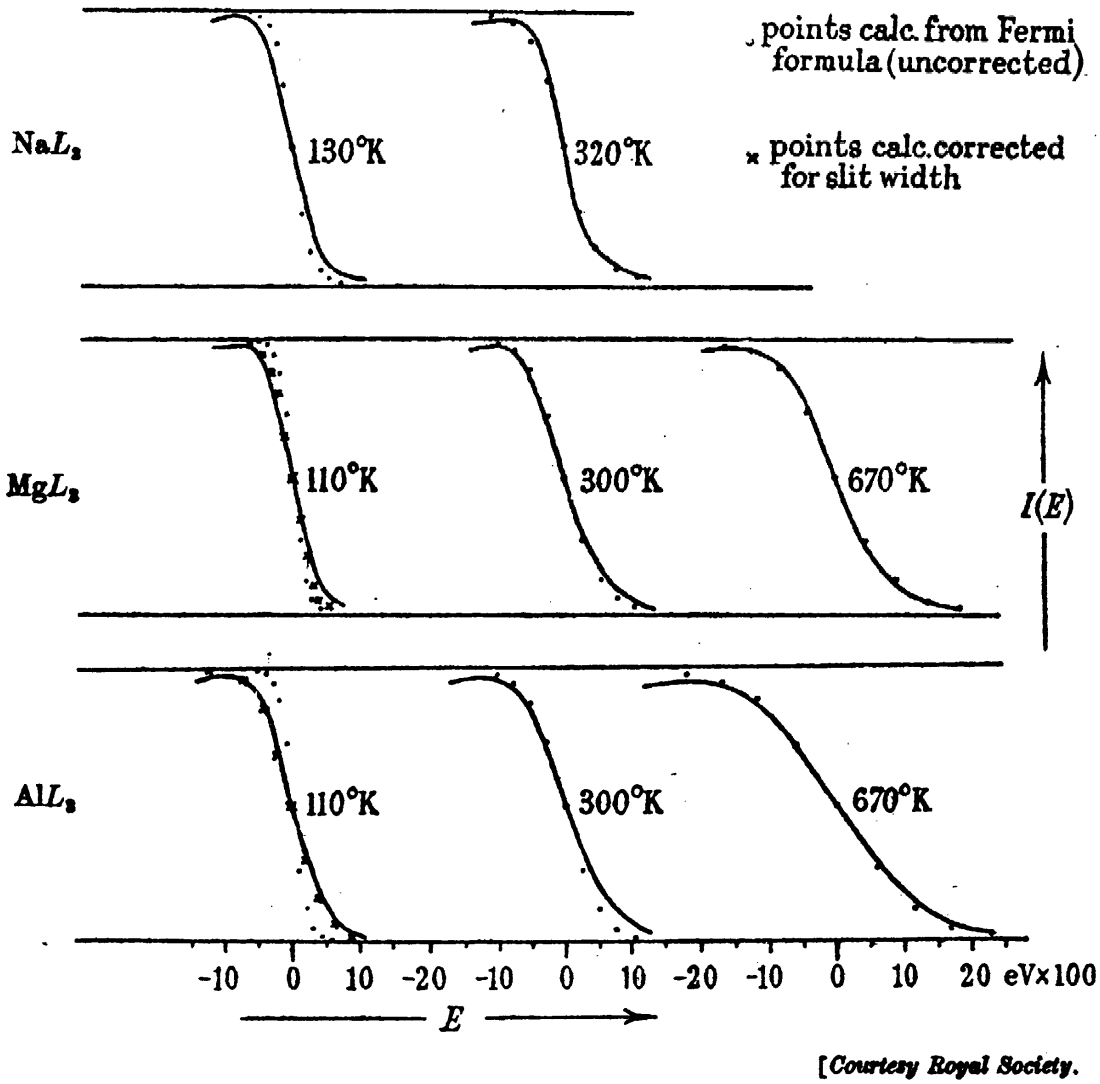
* In this diagram $I(E)$ is the intensity of the radiation in the emitted band in the range of quantum energies E to $(E + dE)$, and ν is the frequency. The quantity $I(E)/\nu^3$ is a measure of the $n(E)$ referred to in the text above; for details see the paper by Skinner referred to on p. 91.

† Strictly speaking the $(2p)$ state has, of course, broadened into a band, but the broadening is so slight that we may talk of a single $(2p)$ state.

‡ The actual $n(E)$ curve does not tail off at the low-energy end of the band.

vertical fall of the curve in Fig. 28(*a*). At higher temperatures some electrons are excited into higher energy states, with the result that the $n(E)$ curve no longer falls so steeply.

As stated above, a metal crystal is to be regarded as containing an immense number of possible electron states, and at the absolute zero an assembly of N valency electrons occupies the $N/2$ lowest electron states of the valency band, each state containing two electrons.



[*Courtesy Royal Society.*

FIG. 30.—Temperature-Broadening of Emission Edges.

The $n(E)$ curves referred to above show the way in which the actual *electrons* in the metal are distributed over the range of energies of the band, but for many purposes it is of interest to know how many *possible energy states* exist in the different regions of energy, and for this purpose $N(E)dE$ may be defined as the number of energy states per unit volume of metal having energies between the limits E and $E + dE$. In this case the $N(E)$ curves show how the possible

energy states are distributed over the ranges of energy concerned, in just the same way that the $n(E)$ curves described above show how the electrons are distributed over the range of energy. As will be seen later, much of the theory has been developed first for the absolute zero of temperature, where the N valency electrons in a crystal occupy the $N/2$ lowest energy states of the valency band. In this case it is customary to draw the $N(E)$ curve and to shade the area of the occupied states. Thus in Fig. 31(a) the $N(E)$ curve shows that the number of states per unit energy range * increases continually, and that the states are fully occupied up to the limit $E = b$, beyond which no states are occupied. In this case the curve in the $N(E)$ diagram is the same as the $n(E)$ curve of Fig. 28(a), except that $n(E) = 2N(E)$, since each state

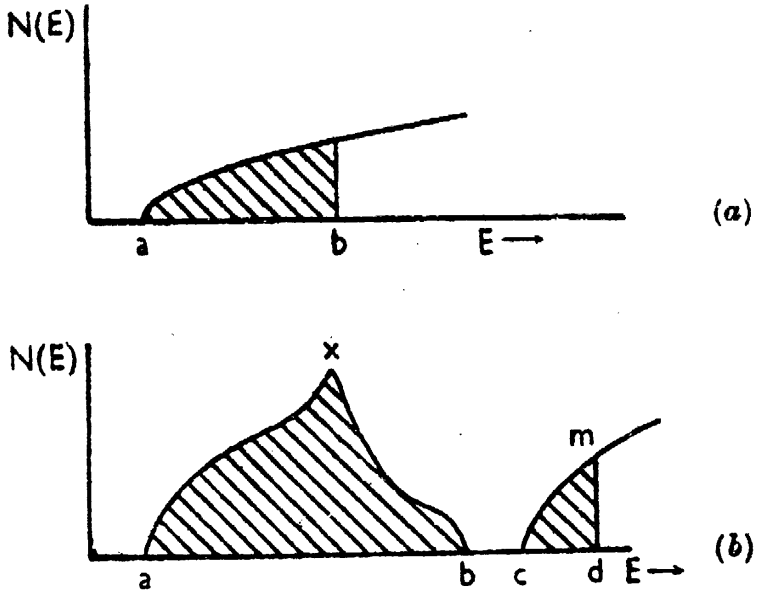


FIG. 31.

contains two electrons. Similarly, the curve of Fig. 31(b) shows that there are possible electron states in the ranges $a \rightarrow b$ and from c onwards, but that there are no states in the range $b \rightarrow c$. Since the $N(E)$ curve rises to a maximum in the region of x, there are far more energy states with energies in the region $E = x$ than at any other values of the energies, and the shaded area which terminates abruptly at $E = md$ indicates that all the electron states up to this point are occupied, and all those beyond are unoccupied. This method of drawing a vertical line at some point of the $N(E)$ curve is, of course, only justifiable for the absolute zero of temperature, where there is a sharp boundary between the occupied and unoccupied states. At higher temperatures the $N(E)$ curve continues to show the distribution of the possible energy

* This is often called the " density of states."

states, but the distribution of the electrons is shown by the $n(E)$ curve. In many books the symbol $N(E)$ is used both for what we have called $n(E)$ and $N(E)$, and the reader must be careful to distinguish between cases where the curves refer to the distribution of electron states and those referring to the distribution of the actual electrons.

The methods of soft X-ray spectroscopy indicate the energy distribution of electrons in solids, and it should be noted that this method by itself begins to give a rough classification of the different types of substances. In Fig. 31(*b*) we have shown an $N(E)$ curve such that there are possible electron states from *a* to *b* and from *c* onwards, but none in the range *b* to *c*, whilst the shaded areas indicate that all the possible states are occupied up to the limit *md*. In such a case we may say that the electrons with energies between *a* and *b* form a closed group which completely fills the first *band* or *zone* of possible energy states, whilst the second zone is only partly filled. In general it may be said that *metals* are characterized by having $N(E)$ curves in which the outermost of the occupied zones is only partly filled, whilst insulators are substances in which the number of electrons is sufficient completely to fill one or more zones, the outermost of which is separated by an energy gap from the next highest zone. If, for example, in Fig. 31(*b*) the number of electrons present had been just sufficient to fill the first zone, *i.e.*, if the region *axb* alone were shaded, the substance would be an insulator (see Part V, p. 195). The technique of soft X-ray spectroscopy is not yet sufficiently developed to give a very sensitive classification of substances, and in the next two chapters we shall therefore indicate briefly the main types of chemical elements as classified empirically and then some of the classes of substance which are of interest in the study of alloys.

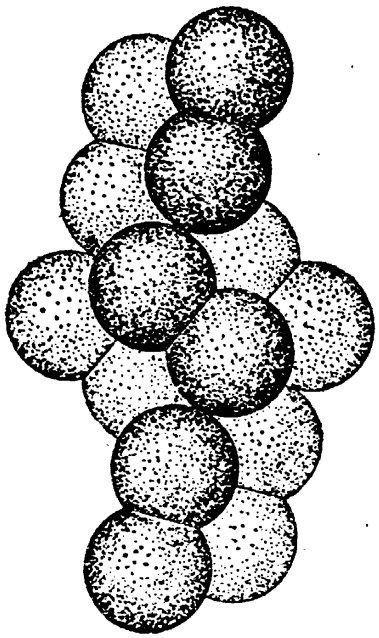
Chapter XIV.—The Elements.

In the preceding pages we have described the energy characteristics of solid metals as these are revealed by the methods of soft X-ray spectroscopy, and it remains to consider the nature of the forces which give rise to cohesion between atoms. The problem of interatomic cohesion is naturally immensely complicated, and includes the whole range of processes from the combination of atoms to form molecules to the formation of liquids or solids from atoms or molecules. In the general case, different processes are superimposed, but fortunately it is possible to find examples where one kind of interatomic force is so predominant that other processes may be ignored; the substance concerned may then be regarded as typical of one kind of interatomic force, and its properties used to study the characteristics of this type of interatomic binding. Proceeding in this way we may recognize the following main types of element as throwing light on the interatomic cohesion with which we are concerned.

The first and most characteristic group of elements is that of the inert gases, helium, neon, argon, krypton, xenon, and emanation. These are monatomic in the gaseous state, and have very low boiling points: He 4° K., Ne 27° K., A 87° K., Kr 121° K., Xe 174° K., Em 212° K. They form no stable chemical compounds, and it is clear that of all the elements they possess the least power of interatomic cohesion. In Part II we have seen that complete octets of electrons in free atoms form very stable groups, and it has long been recognized that the properties of the inert gases are due to their atoms having outer groups of eight electrons. These groups of eight electrons (or two in the case of helium) are so stable that they are only very slightly affected by the presence of other atoms, and the motion of their constituent electrons cannot be changed sufficiently to give rise to strong binding forces. The forces which bind the atoms of inert gases together to form the liquid or the solid state are the so-called van der Waals Forces, and are described later (p. 121).

The next group consists of the elements immediately preceding the inert gases, and these fall into two main classes. The elements hydrogen, nitrogen, oxygen, and fluorine form very stable diatomic molecules and have low boiling and melting points. G. N. Lewis (1916) first suggested that in molecules of this type the interatomic forces were due to the sharing of electrons, so that each atom acquired a full complement of eight electrons (or two in the case of hydrogen). In fluorine, for

example, each atom possesses seven electrons, and in the diatomic molecule it is regarded as sharing one electron with its neighbour and so obtaining a stable octet. Similarly, in the O_2 molecule each oxygen atom shares two electrons, and in the N_2 molecule each nitrogen atom shares three electrons, and in this way stable octets are built up. The low boiling points of these gases are the result of the fact that when once the atom has acquired its octet, the group of electrons is so stable that its electrons cannot give rise to further bonding, and the forces between the molecules in liquid and solid hydrogen, nitrogen, oxygen, or fluorine are again of the van der Waals type. The kind of atomic linkage due to electron sharing is called *homopolar* or co-valent bonding, and is found in many other substances, although the boiling points may be very much higher, and their other properties very different from those of hydrogen, nitrogen, oxygen, or fluorine.



[*Courtesy Reinhold Publishing Corp.*

FIG. 32.—The Crystal Structure of Iodine, Showing the Presence of Pairs of Atoms Formed by Diatomic I_2 Molecules.

Fluorine is the first member of the halogen family, and the remaining halogens, chlorine, bromine, and iodine all form stable diatomic molecules, whilst the melting points and boiling points rise with increasing atomic number. Here the diatomic molecules are again formed by simple homopolar bonds, and the forces which hold the molecules to one another in the liquid or solid are of the van der Waals type, which clearly becomes much more pronounced as the atomic number increases—iodine is a solid at room temperature. Fig. 32 shows the crystal structure of iodine, and here it is clearly possible to recognize the diatomic molecules, the distances between two atoms in a molecule being considerably smaller than the remaining interatomic distances. The crystal structures of the remaining halogens are different, but so far as they have been determined they all contain diatomic molecules, and they may all be regarded as structures where homopolar bonding produces diatomic molecules which are themselves held together by van der Waals forces.

When we turn to the remaining elements of Groups VB and VIB, we find that arsenic, antimony, bismuth, sulphur, selenium, and tellurium in the gaseous state can all form stable diatomic molecules, but more complicated molecules (*e.g.*, S_8, As_4) are also found, whilst the solid state is much more stable; antimony, for example, has a melting

point of 630° C. The crystal structures of arsenic, antimony, bismuth, selenium, and tellurium * are of great interest, because they illustrate what has been called the $(8 - N)$ rule. In the halogens we have seen that the crystal structures show diatomic molecules, in which each atom shares an electron with its one close neighbour and thereby builds up a complete octet. The crystal structure of the Group VI elements selenium and tellurium is shown in Fig. 33 and here it will be seen that atoms form spiral chains in which each atom has two close neighbours, the remaining interatomic distances being considerably greater. This clearly suggests that in these crystals each atom is building up an octet of electrons by sharing one electron with each of its two close neighbours to form normal co-valent bonds. The crystal structure of arsenic,

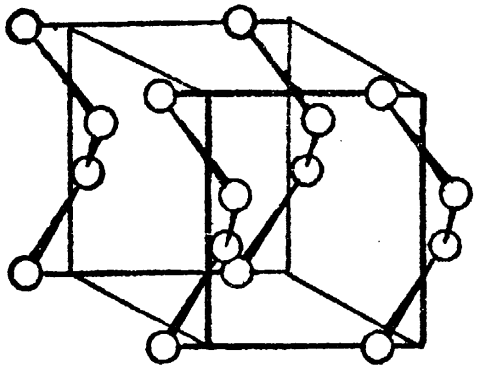


FIG. 33.—The Crystal Structure of Tellurium, Showing the Spiral Chains of Atoms in which Each Atom has Two Close Neighbours.

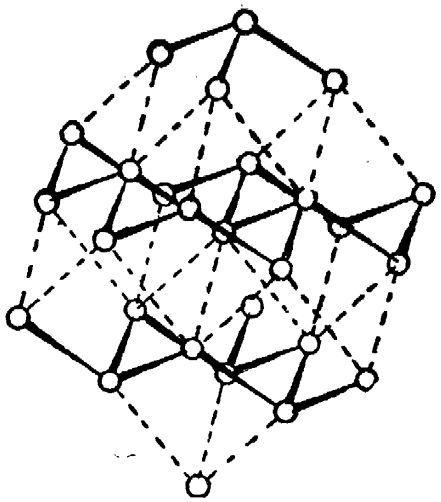


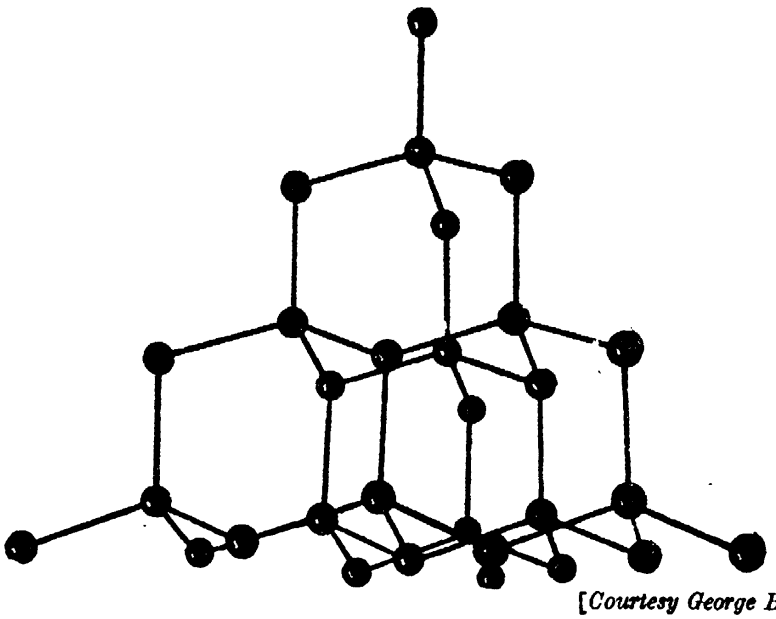
FIG. 34.—The Crystal Structure of Antimony, Showing the Double Layers of Atoms, in which Each Atom has Three Close Neighbours, and Three at a Greater Distance in the Next Layer.

antimony, and bismuth in Group V is shown in Fig. 34, and here it will be seen that the structure consists of double layers in which each atom has three close neighbours. Since the atoms of the elements of Group VB contain 5 electrons, they require 3 more electrons to complete an octet, and the crystal structure suggests clearly that this is accomplished by each atom forming three normal co-valent bonds and sharing one electron with each of its three close neighbours. It will be seen that if N is the number of the group in the Periodic Table, these crystal struc-

* The structures of sulphur and phosphorus are more complicated, but we omit these because they are non-metallic. The structure of black phosphorus is different from that of arsenic, but is such that each atom has three close neighbours. The structure of rhombic sulphur contains S_8 molecules in the form of closed puckered rings in which each atom has two close neighbours. These structures are thus further examples of the $(8 - N)$ rule.

tures, and those of the halogens, are characterized by the fact that each atom has $(8-N)$ close neighbours. In these structures we may regard the chains of tellurium atoms and the double layers of antimony atoms as constituting immense molecules in which the atoms are held together by simple co-valent linkages. The nature of the forces which bind the chains or double layers to one another is not so well understood. According to one point of view these forces are of the van der Waals type, whilst another interpretation is that they resemble the cohesive forces in metals (see p. 282). Whatever view is adopted, the important thing to recognize is that in crystals such as those of tellurium and antimony, two distinct kinds of cohesive force exist.

According to the $(8-N)$ rule, the elements of Group IVB should crys-



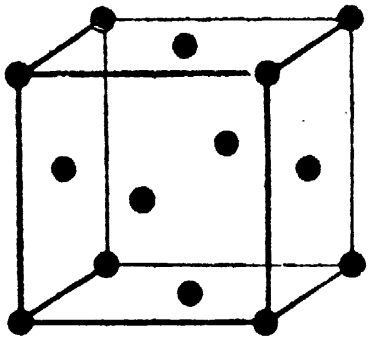
[*Courtesy George Bell and Sons.*

FIG. 35.—The Crystal Structure of the Diamond, Showing how Each Atom has Four Equidistant Neighbours.

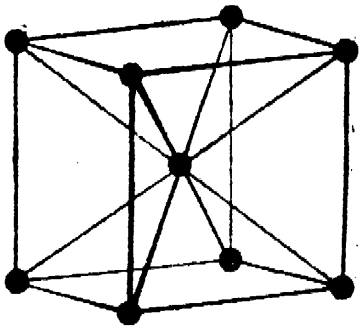
tallize so that each atom has $8 - 4 = 4$ close neighbours. Here we find that carbon (diamond), silicon, germanium, and grey tin crystallize in the well-known diamond type of structure in which each atom has four close neighbours arranged tetrahedrally, as shown in Fig. 35. In this case we are to regard the whole crystal as constituting an immense co-valent molecule, in which each atom builds up an octet of electrons by sharing one electron with each of its four neighbours. It will be noted that the stability of these co-valent bonds decreases with increasing atomic number, as can be seen from the following list of melting points:

Diamond	3572° C.
Silicon	1421° C.
Germanium	958° C.
Grey tin	Stable only at low temperatures.

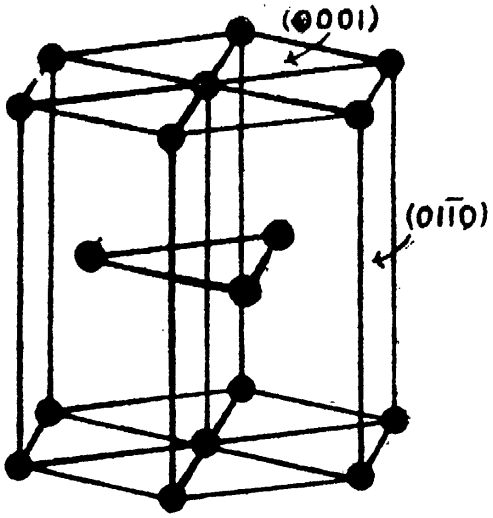
The same principle applies to the co-valent bonds in the crystals of the antimony, tellurium, and iodine types. Thus the co-valent linkages between the atoms in the iodine I_2 molecules are weaker than those in bromine Br_2 molecules, and the co-valent linkages between adjacent atoms in the spiral chains of tellurium (Fig. 33) and the double layers of antimony (Fig. 34) are weaker than the corresponding bonds in selenium and arsenic. The van der Waals forces between the molecules do not, however, behave so simply; thus iodine is a solid, and bromine



Face-centred cube.



Body-centred cube.



The close-packed hexagonal structure with axial ratio 1·633.

FIG. 36.—The Three Typical Metallic Structures.

a liquid at room temperatures, but bismuth has a lower melting point than antimony.

It is to be noted that crystals which possess structures of the $(8-N)$ rule type are either insulators or "semi-conductors." Thus diamond is an insulator, whilst silicon shows a metallic lustre and possesses a slight electrical conductivity, but the conductivity increases with rise of temperature in contrast to the behaviour of normal metals.* On

* In a semi-conductor the resistance decreases when small amounts of impurity enter into solid solution, whereas in a normal metal the resistance diminishes with increasing purity.

moving back to Groups IIIB, IIB, and IB of the Periodic Table and then to the transition elements and elements of the A sub-groups, we find that with the exception of boron all * these elements are true metals which conduct electricity and have normal temperature coefficients of resistance, *i.e.*, the resistance increases as the temperature rises. With a few exceptions these elements crystallize in one of the three typical metallic structures, the face-centred cubic, body-centred cubic, and the close-packed hexagonal structures which are shown in Fig. 36. In the transition elements and those of the A sub-groups, manganese, uranium, and one form of tungsten crystallize in very complicated structures, and all of the remaining elements crystallize in one of three typical structures shown in Fig. 36. In the B sub-groups zinc and cadmium crystallize in a curious modification of the close-packed hexagonal structure which is shown in Fig. 37. This is similar to the normal close-packed hexagonal structure, except that it is extended in the direction of the *c*-axis, so that the axial ratio † is much greater than that for close-packed spheres (1·633). Each atom has six close neighbours in the basal plane and six others at a greater distance, three in the layer above and three below. Mercury does not crystallize in this structure, but forms instead a simple rhombohedral structure as shown in Fig. 38. Here again each atom has six close neighbours, so that, considered empirically, the $(8-N)$ rule applies to the elements of Group IIB as well as to those of Groups VB, VIB, and VIIB and the earlier members of Group IVB. There can, however, be no question of the formation of simple co-valent linkages in the crystals of zinc, cadmium, and mercury, because, since each atom has only two electrons, there are insufficient electrons to form six co-valent bonds per atom. The metallic properties of these three elements are also normal.

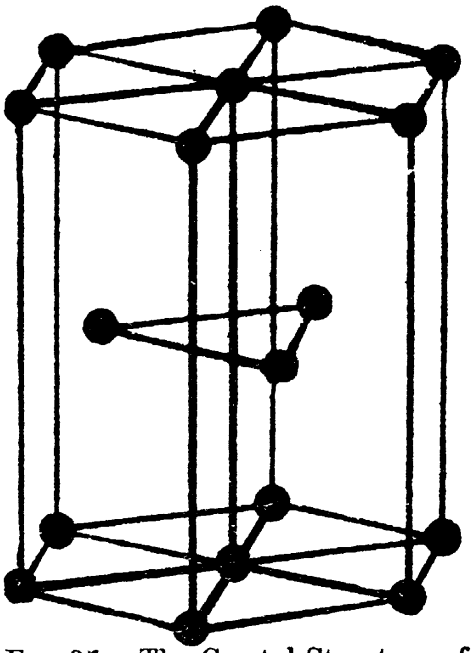


FIG. 37.—The Crystal Structure of Zinc with Axial Ratio 1·856.

In Group IIIB, gallium forms an abnormal crystal structure. Indium crystallizes in a face-centred tetragonal structure, but as can be

* It is possible that uranium is only pseudo-metallic.

† If c is the height of the unit cell in Figs. 36 and 37, and a is the side of the hexagon in the basal plane, the axial ratio is equal to c/a. For close-packed spheres the axial ratio equals $\sqrt{\frac{8}{3}} = 1{\cdot}633$.

seen from Fig. 39, the axial ratio, c/a, is very nearly unity, so that the structure is really only a very slightly distorted form of the typical face-centred cube. The next member of the sub-group, thallium, crystallizes in typical metallic structures, and the same applies to lead in Group IVB, although white tin has an abnormal structure.

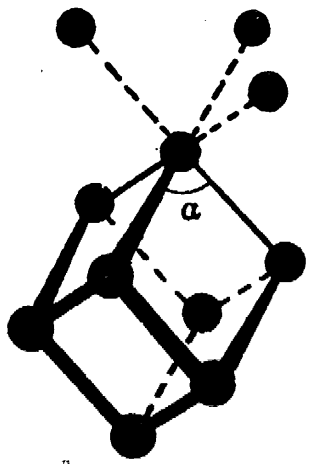
It will be seen, therefore, that when the elements are surveyed as a whole, they fall into four main classes :

(1) The inert gases.

(2) The elements hydrogen, nitrogen, and oxygen, which form very stable diatomic molecules and exist as gases down to very low temperatures.

(3) The elements preceding the inert gases. These form diatomic, and often more complex, molecules in the gaseous state and crystallize according to the $(8-N)$ rule, so that their valencies are satisfied in the solid crystal. These are insulators or semiconductors.

(4) The metals, which nearly all crystallize in one or more of the three typical metallic structures.

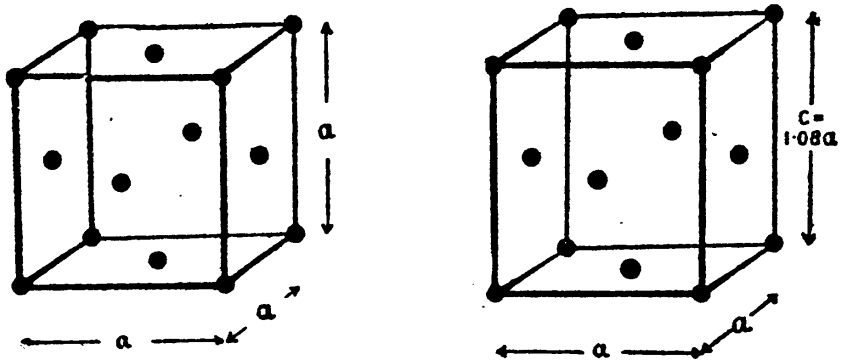


$a = 70° 31{\cdot}7'$.

FIG. 38.—The Crystal Structure of Mercury.

One cell of the simple rhombohedral structure is shown. There is one atom at each corner of this cell, and three atoms from adjacent cells have been included in order to show each atom has six equidistant neighbours.

It will be noted that in the First Long Period of the Table of the Elements, germanium crystallizes in the diamond type of structure.



Face-Centred Cube. Indium Structure.

FIG. 39.

In the next Period, the modification of tin (grey tin) which crystallizes in this structure is stable only at low temperatures, whilst in the Third Long Period, lead does not crystallize in this structure at all, but forms a face-centred cubic structure. The reason for this difference is to be

found in the relative stabilities of the $(4s)^2$, $(5s)^2$, and $(6s)^2$ sub-groups of electrons which has already been discussed in Chapter X (p. 57). The results of X-ray crystal structure analysis show that the closest distances of approach of the atoms in thallium and lead (*ca.* 3·5 A.) are considerably greater than that in gold (2·88 A.), whereas the closest interatomic distances in gallium and germanium are slightly less than that in copper. This suggests clearly * that in thallium and lead the $(6s)^2$ sub-group of electrons is sufficiently stable to persist in the solid crystals of these elements, so that thallium and lead in the crystalline state are analogous to univalent and divalent metals respectively, rather than to trivalent and tetravalent elements; this explains why lead does not crystallize in the diamond structure, which, of course, involves four valency electrons per atom. A similar study of interatomic distances suggests that this process of incomplete ionization is present to some extent in indium and white tin, and in considering the different metals it is convenient to regard the four metals indium, tin (in the white modification), thallium, and lead as forming a small class characterized by incomplete ionization of the $(ns)^2$ sub-group of electrons. It must, however, be emphasized that this is a characteristic of the crystals of the elements, and that in many of their alloys these metals may act according to their normal valencies of three and four; *e.g.*, when thallium dissolves in solid magnesium, it does so as a typical trivalent element.

* The general effect of increasing atomic number is to attract the electrons more closely to the atoms. We therefore expect increasing atomic number to result in a closer distance of approach of atoms, unless a new group, or sub-group, is built up sufficiently to produce repulsion.

Chapter XV.—Assemblies of Unlike Atoms.

The Ionic Bond.

The preceding section has dealt with the characteristics of the elements, and we have now to consider the classes of substances which are found when two or more elements unite to form a system. In the case of the elements we have seen that the interatomic forces can be divided into the three main classes: (*a*) van der Waals Forces, (*b*) co-valent bonds, and (*c*) metallic linkages. When we consider the forces which exist between unlike atoms in solid or liquid solutions, compound molecules, &c., examples of all the above types are found, but apart from these a new type of interatomic force is met with, namely the *ionic* or polar bond. We have already seen that the inert gases correspond with very stable groupings of electrons. An atom of sodium has one valency electron outside a stable group of eight, whilst an atom of chlorine has seven valency electrons, and thus needs one electron to complete a group of eight. In this case chemical combination occurs by the sodium atom giving up its valency electron to the chlorine atom so that the latter acquires a complete group of eight electrons. The resulting compound is said to be polar or ionic, since the transference of the electron from one atom to another produces a positive and a negative ion, and these are held together by their mutual electrostatic attraction which pulls the ions together until the attractive force is balanced by the repulsion produced when the electron clouds of the ions overlap. Since the resulting molecules consist of a positive and a negative ion, they possess a relatively large dipole moment,* in contrast to co-valent molecules such as H_2, where the electron cloud of the valency electrons is much more uniformly distributed between the two atoms.

* Two equal and opposite charges, $+e$ and $-e$, separated by a distance l, form an electrical dipole whose moment, μ, is defined by the relation $\mu = el$. In a molecule we can only obtain the probable electron distribution or electron density in the space surrounding the nuclei, and if the molecule is asymmetric, the charge distribution will in general possess a permanent electric moment, or dipole moment, which can be measured experimentally. Interatomic distances in molecules are of the order of 10^{-8} cm., and since the electronic charge $e = 4{\cdot}77 \times 10^{-10}$ e.s.u., molecular dipole moments are of the order of 10^{-18} e.s.u., and this quantity is called a *debye*. The dipole moment of the HCl molecule may be written $\overset{+}{H}\overset{\rightarrow}{Cl} = 1{\cdot}04$ debyes, where the arrow indicates that the negative charge is at the chlorine end of the molecule. It should be appreciated that when a co-valent bond is formed by electron sharing, the shared electrons may spend a greater proportion of their time near to the one atom (A) than to the other (B), and in this case the atom A will be associated with a negative charge; the concept of shared electrons does not imply that the electrons are associated equally with the two atoms concerned.

The crystal structure of sodium chloride is shown in Fig. 40. Here it will be seen that all trace of diatomic Na^+Cl^- molecules has disappeared, and the structure consists of an array of positive and negative ions which are held in contact by their mutual electrostatic attraction, and held apart by the repulsion which results from the overlapping of the electron clouds of the ions. Magnesium oxide, $Mg^{++}O^{--}$, also possesses the NaCl type of structure; here the divalent magnesium atoms have each given up two electrons to the oxygen atoms, which thereby acquire complete groups of 8 electrons. Since the ions in MgO are doubly charged, we can understand why the cohesion in magnesium oxide is much stronger than in sodium chloride, and the high melting point of magnesia is the result of this increased attraction. A very satisfactory theory of the properties of simple polar structures of this kind has been developed by Born and others. In this work the potential energy of the crystal is written in the form :

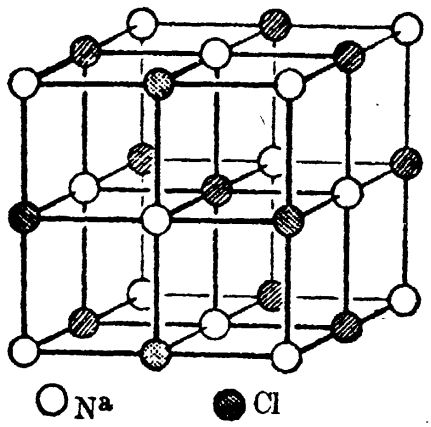


FIG. 40.—Sodium Chloride.

$$\Phi = -\frac{a}{r} + \frac{b}{r^n}.$$

Here the first term is the potential energy resulting from an electrostatic attraction varying as the inverse square of the distance (r) between the ions, and the constant a can be calculated for the different types of crystal structure. The second term is purely empirical and represents a repulsion. Comparison with experimental values of various physical properties requires the constant n to be of the order of 10 for salts, so that the repulsion increases very rapidly at small distances. Later developments of the theory indicate that a repulsion term of the form $e^{-r/a}$ is more probable.

From the point of view of the theory of metals, it is important to realize that there is an almost continuous transition from typical ionic compounds such as those described above, to the purely metallic linkage of normal metals. There is, for example, a whole series of compounds such as MgO, MgS, MgSe, MgTe, MnSe, PbSe, all of which crystallize in the NaCl type of structure. For these it is a general principle that the compound is more stable, and its melting point higher, the more electropositive the metal and the more electronegative the element from Group VI. Similar considerations apply in other cases. Thus the compound CaF_2 has the crystal structure shown in Fig. 41, and this is anti-isomorphous * with the crystal structures formed by the com-

* *I.e.*, the metal ions in CaF_2 occupy the positions of the negative ions in Mg_2Si.

pounds Mg_2Si, Mg_2Ge, Mg_2Sn, and Mg_2Pb. Here again the melting points fall as the metalloid element becomes less electronegative, so that Mg_2Pb has the lowest and Mg_2Si the highest melting point of the series. These compounds have a metallic lustre and a slight electrical conductivity, although they are semi-conductors in the sense that the resistance decreases with rise of temperature.

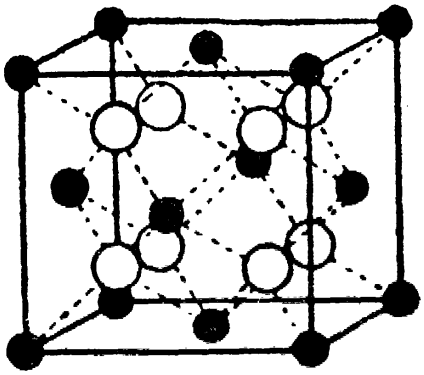
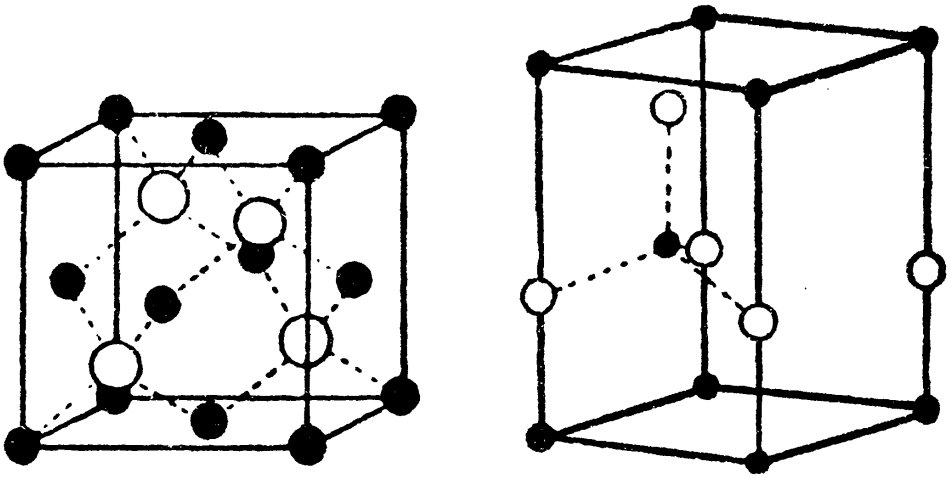


FIG. 41.—Calcium Fluoride.

The above intermetallic compounds can readily be understood as a continuation of the typical ionic compounds into the region of weakly electronegative elements, and it will be noted that they have the formulæ to be expected from the normal valencies of the elements concerned. Compounds of this kind are often formed when one element is very electropositive compared with the other, and they may be regarded as the result of an electrochemical factor. Even in cases where definite compounds do not exist, the electrochemical factor may exert an important influence on the type of alloy structure formed, and some of these effects are discussed below.

Co-Valency Compounds.

Turning from the effects of polar or ionic bonding to that of co-valent bonding, it is, of course, well known that the idea of electron sharing introduced by G. N. Lewis and developed in terms of quantum



Zinc Blende. Wurtzite.

FIG. 42.

mechanics, has explained the structures of many chemical compounds. This work has been discussed in many books, and we shall, therefore, not deal with it here.* We may note that just as the structure of the

* The reader may consult N. V. Sidgwick's "Co-valent Link in Chemistry" and L. Pauling's "The Nature of the Chemical Bond."

diamond is one immense molecule in which each atom exerts its normal valency of four, so crystals with this, or a similar structure, are formed by combinations of atoms, provided that the average number of valency electrons per atom is four. Fig. 42 shows the zinc blende and wurtzite structures, which are characterized by each atom having four neighbours arranged tetrahedrally. Here we find the zinc-blende structure is formed by a whole series of compounds, such as GaAs, CdSe, and CuBr, in which the characteristic is that there are eight valency electrons to two atoms, so that the ratio of four valency electrons to one atom is preserved. Some of these compounds show metallic properties, and, just as in the case of the ionic and metallic bonds, we cannot draw any hard and fast line between the metallic and co-valent linkage, and it is very probable that in many intermetallic phases forces of a partly co-valent nature are present.

Alloy Structures : Primary Solid Solutions.

Before proceeding further it is convenient to review briefly the types of phase usually encountered in alloys, and for this purpose we have reproduced the equilibrium diagram of the system copper–zinc in Fig. 43. We shall assume that the reader is familiar with diagrams of this kind,* showing the phases which exist in alloys of different compositions when they are in equilibrium at different temperatures. It will be seen that the copper-rich alloys of this system consist of the α-solid solution of zinc in copper, whilst at the zinc-rich end of the system there is a narrow range of solid solution of copper in zinc. Solid solutions of this kind may be called *Primary Solid Solutions* or *Terminal Solid Solutions*, and they retain the crystal structure of the parent metal. These primary solid solutions are of two types, the so-called *substitutional* and *interstitial* solid solutions. In the interstitial solid solutions, the solute atoms fit into the interstices or spaces between the atoms of the solvent. This kind of solid solution is naturally confined to systems where one atom is very much smaller than the other. The most important example is the solid solution of carbon in γ-iron, which forms the basis of the steels, whilst boron and nitrogen can also form interstitial solid solutions with some transition elements.

In the more general case of substitutional solid solutions the solute atoms replace those of the solvent, so that the two kinds of atom are situated on a common lattice. It is only natural that the formation of an appreciable range of substitutional solid solution is confined to cases where the two kinds of atoms do not differ too greatly in size, and this is

* Reference may be made to C. H. Desch, "Metallography," or W. Rosenhain and J. L. Haughton, "An Introduction to the Study of Physical Metallurgy."

confirmed experimentally. It might at first be thought that the modern picture of an atom would make it impossible to allot any definite size to the atom of a particular element, since the electron cloud has no sharp boundary. Actually, however, considerable progress has been made by assuming that the "atomic diameter" of an element is given by the closest distance of approach between two atoms in the crystal of the

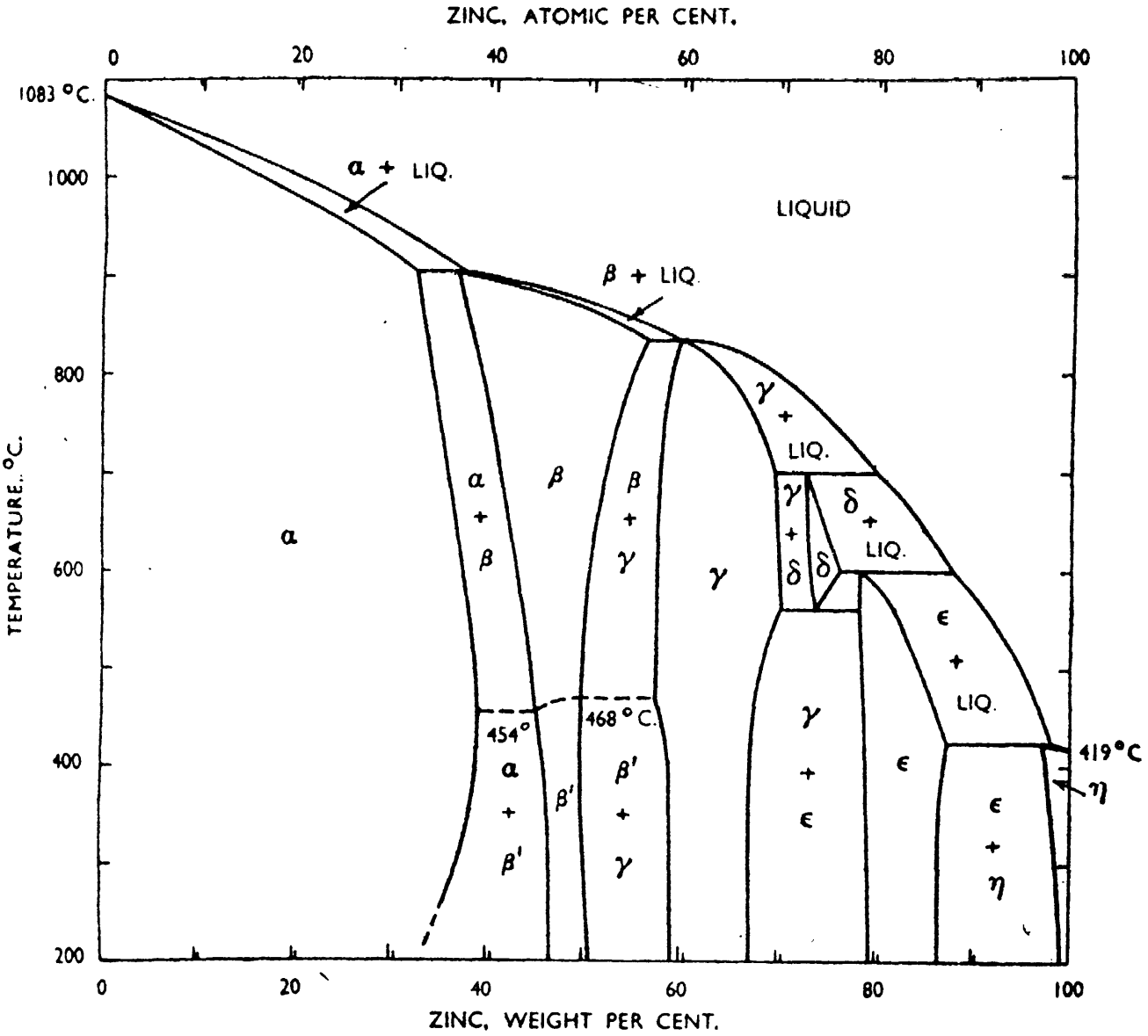


FIG. 43.—Equilibrium Diagram of the System Copper–Zinc.

element. It was first shown by Hume-Rothery, Mabbott, and Channel-Evans (1934) that if the atomic diameters are defined in this way,* the solid solubility of one element in another becomes very restricted if the atomic diameters of the two elements concerned differ by more than about 15%, whilst within this range solid solutions may be formed provided that other factors are favourable. This principle requires ampli-

* See Fig. 93, p. 216.

fication in the case of elements such as lead which may change their state on entering into solid solutions (see p. 104), and also with some elements such as gallium where an abnormal crystal structure gives one very close distance of approach of the atoms; but in general the principle of what may be called favourable and unfavourable size-factors is well established. In view of frequent misunderstanding, it must be emphasized that considerations of atomic diameters alone do not enable one to predict that one metal will dissolve in another in the solid state. This will readily be appreciated from Fig. 43, where there is a wide solid solution of zinc in copper, but only a very restricted solid solution of copper in zinc. The concept of a favourable size-factor is thus most useful as a preliminary test which must be satisfied if there is to be any chance for one metal to dissolve appreciably in another, but whether a solid solution is actually formed is often controlled by other factors. Of these, the one most readily understood is that if the two metals differ greatly in the electrochemical series, there is a very general tendency for them to form stable intermetallic compounds at the expense of the primary solid solutions.

The extent of primary solid solutions varies from complete miscibility in the solid state, as in the systems silver–gold and copper–nickel, to a solubility which is too small to be measured, and whose presence can only be deduced indirectly. Primary solid solutions at high temperatures are usually described as having a random arrangement of the different kinds of atoms on the common lattice, and this is true in the sense that there is no regular arrangement of the two kinds of atoms which extends over distances large compared with the atomic diameter. It is, however, almost certain that in most primary solid solutions there is a short-range order, in the sense that a given atom tends to have more neighbours of the opposite kind than would result from a purely random distribution. The evidence for this is at present indirect, but short-range order is undoubtedly present in some cases, and is favoured by increasing electrochemical factor.

Alloy Structures: Superlattices.

In cases where the primary solid solution is of wide extent, there is a very general tendency for alloys in the regions of 25 and 50 at.-% of solute, on slow cooling or on annealing at a low temperature, to undergo an atomic re-arrangement in which, although the structure as a whole remains that of the solvent, the two kinds of atoms occupy definite positions relative to one another, so that long-range order is established. In the system copper–gold, for example, the alloy of composition Cu_3Au consists at high temperatures of a disordered face-

centred cubic structure, but on slow cooling the two kinds of atoms arrange themselves as shown in Fig. 44. This kind of structure is called a *Superlattice*, and is usually characterized by a tendency for the solute atoms to keep as far away from one another as possible.* The formation of a superlattice may be regarded as a process in which the lattice strain produced by the solute element in the random solid solution is reduced by the formation of an ordered structure. It is therefore natural that, provided the solvent and solute atoms are of sufficiently similar size to permit the formation of a wide solid solution, the tendency to form superlattices increases with increasing difference in atomic diameters, since the greater this difference, the greater the strain to be relieved. Thus, superlattices are found in the system copper–gold, where the atomic diameters are Cu = 2·54 A., Au = 2·88 A., but not in the system silver–gold, where the sizes of the two atoms are nearly the

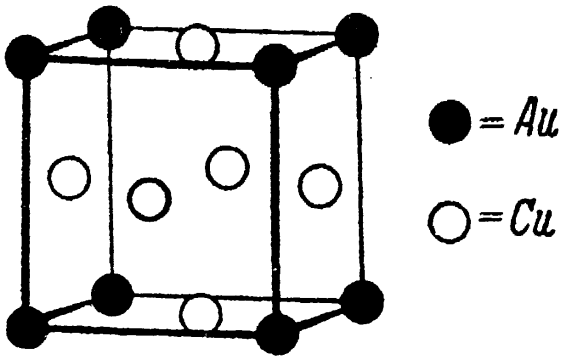


FIG. 44.—The Cu_3Au Superlattice Structure.

same. But apart from this simple effect of atomic diameter, the formation of a superlattice is favoured by increasing electrochemical factor. It is probable, therefore, that there is a continuous range from superlattices involving only the metallic bond, and formed merely to relieve the lattice strain resulting from atoms of unequal size, to superlattices with increasing degrees of ionic bonding, and the presence of bonding of a partly ionic nature in solid solutions must always be borne in mind. Up to the present, this phenomenon has not been developed mathematically.

Alloy Structures: Intermediate Phases.

Reference to Fig. 43 will show that in the system copper–zinc increasing zinc content results in the primary α-solid solution being succeeded by a two-phase region. There is then a homogeneous region, denoted β, the composition of which is in the region of 50 at.-%

* This principle has been discussed by W. Hume-Rothery and H. M. Powell, *Z. Krist.*, 1935, **91**, 23.

of zinc (CuZn). This has a disordered body-centred cubic structure at high temperatures, and at low temperatures an ordered body-centred cubic structure of the cæsium chloride type. The change from order to disorder takes place in the neighbourhood of 460° C., and is a simple superlattice transformation. At higher percentages of zinc there is a phase denoted γ with a characteristic type of structure, and then the ε-phase, which has a close-packed hexagonal structure. The mean composition of the ε-phase is about 82 at.-% of zinc, whilst its boundary on the copper-rich side is at about 79 at.-% of zinc. In the system copper–zinc the intermediate phases are all of variable composition, but in many alloy systems intermediate phases are found, the composition of which is fixed, or at any rate varies over such a narrow range that no variation can be detected experimentally. Such phases are usually called intermetallic compounds, and their composition generally corresponds with a reasonably simple whole-number ratio of the constituent atoms. Considerable discussion has taken place as to whether the intermediate phases of variable composition are to be regarded as intermetallic compounds,* and to some extent this is a matter of definition. If we regard a metal as an assembly of positive ions held together by the attraction of the shared valency electrons, it will be appreciated that a crystal of a metallic element is itself a giant molecule, in which the atoms or ions are held together by the shared electrons. From this point of view all the phases in alloy systems, including the primary solid solutions, are to be regarded as involving chemical combination of one kind or another, although some of them may not correspond with the formation of polyatomic molecules in the liquid or vapour states. If, on the other hand, we prefer to regard the metallic linkage as something distinct, then there is no reason why some intermediate phases, although differing in crystal structure from the parent metals, should not have their atoms held together by purely metallic linkages, and we may expect a continuous transition from purely metallic intermediate phases to those involving ionic or co-valent bonds.

In the great majority of cases, the formulæ of intermetallic compounds do not agree with those to be expected from the normal principles of valency, and this is readily understood when it is remembered that these phases are often normal conductors of electricity. We have already seen that in the ionic and co-valent compounds the electrons tend to be bound into stable groups, and the ordinary principles of

* The usual text-book distinction between mixtures and compounds does not take into account the possibility of a compound forming a solid solution with its constituent elements.

valency are the result of the fact that definite numbers of electrons form stable groupings. Consequently, if free electrons are to be left to give the substance metallic properties, the combining ratios must in general be different from those in the normal compounds of chemistry, where all the valency electrons form stable groups, so that the metallic properties are lost.

The Science of Alloy Structures is at present comparatively undeveloped, but it has been possible to understand some of the principles concerned. In the first place, as we have explained above, when two metals differ markedly in electrochemical characteristics there is a general tendency to form stable compounds, many of which have the formulæ to be expected from the normal valencies, and which may be regarded as an extension of the simple ionic or co-valent compounds into the region of the weakly electronegative elements, *e.g.*, compounds such as Mg_2Sn and Mg_3Sb_2. In the second place, some intermediate phases have been shown to have structures which are clearly determined to a large degree by the relative sizes of the atoms concerned. For example, the so-called Cu_2Mg type of structure is formed by Cu_2Mg, W_2Zr, KBi_2, and Au_2Bi; here an approximately constant ratio of atomic diameters is shown, and it is particularly interesting to note that the bismuth atom can play the part of the smaller atom in KBi_2, and of the larger atom in Au_2Bi. In the same way the ternary aluminium–copper–magnesium alloys give rise to a phase of composition approximately $Mg_3Cu_7Al_{10}$ and this is isomorphous with the phase Mg_2Zn_{11} in the binary system magnesium–zinc. The characteristic here is an approximately constant ratio of large magnesium atoms to small atoms of copper, aluminium, or zinc, since Mg_2Zn_{11} has 33 small atoms to 6 large magnesium atoms, whilst in $Mg_3Cu_7Al_{10}$ there are 34 small atoms to 6 large magnesium atoms. The determination of crystal structure by X-ray diffraction methods has enabled several groups of intermetallic phases to be classified in this way, but up to the present it has not been possible to understand the other factors which are concerned; so that one cannot yet explain why the above types of structure, for example, are formed in some alloy systems but not in others where the atomic diameters have the ratio which is clearly the main characteristic of the structure.

Alloy Structures : Electron Compounds.

We have discussed above the main characteristics of the system copper–zinc, whose equilibrium diagram is shown in Fig. 43, and examination has shown that alloys with somewhat similar characteristics are formed by many alloys of copper, silver, and gold with the elements

of the earlier B Sub-Groups of the Periodic Table, as well as with beryllium, magnesium, aluminium, and silicon. Thus Fig. 45 shows the equilibrium diagram of the system copper–gallium, where there is a body-centred cubic β-phase stable only at high temperatures, whilst a phase with the "γ-brass" structure appears at higher concentrations of gallium. It will be seen that the β-phase lies in the region of 25 at.-% of gallium (Cu_3Ga), and that at low temperatures there is a close-packed hexagonal phase at roughly the same composition. Comparison of Figs. 43 and 45 will show that on passing from zinc to gallium the proportion of the solute metal contained in the β-phase becomes less. The first step towards an understanding of this class of alloy was made in 1926 when Hume-Rothery * pointed out that the compositions of the β-phases in some of those alloys had the common characteristic that they corresponded to a ratio of 3 valency electrons to 2 atoms. In the systems copper–zinc, copper–aluminium, and copper–tin, the compositions of the β-phase are near to those given by the formulæ CuZn, Cu_3Al, and Cu_5Sn, and it will be seen that if copper, zinc, aluminium, and tin are given their normal valencies of 1, 2, 3, and 4 respectively, these compositions all correspond with a ratio of 3 valency electrons to 2 atoms. This principle was then confirmed and extended by the remarkable X-ray work of Westgren and his collaborators which showed that in alloys of copper, silver, and gold, body-centred cubic, γ-brass, and close-packed hexagonal structures tended to occur at electron : atom ratios of 3 : 2, 21 : 13, and 7 : 4 respectively. The electron concentration 3 : 2 also tends to give rise to phases with structures similar to that of β-manganese, or of the close-packed hexagonal type, and in some systems the body-centred cubic phase is stable at high temperatures, and at low temperatures a β-manganese (*e.g.*, Ag_3Al) or close-packed hexagonal (*e.g.*, Cu_3Ga) phase is formed. Later work by Ekman † showed that similar structures were formed in some alloys of the transition elements, provided that these were regarded as possessing a zero valency. Thus in the systems nickel–zinc and iron–zinc, phases with γ-brass structures occur at the compositions Ni_5Zn_{21} and Fe_5Zn_{21}, so that the ratio of valency electrons to atoms, which may be called the ***electron concentration***, is 42 : 26, or 21 : 13. It was further shown by Bradley and Gregory that in ternary copper–zinc–aluminium alloys, the typical γ-brass structure could be obtained if the proportions of the elements were adjusted so as to maintain the electron concentration at the required value 21 : 13. Later, Hume-Rothery, Mabbott, and Channel-Evans showed that where the

* *J. Inst. Metals.* 1926, **35**, 309.
† *Z. physikal. Chem.*, 1931, [B], **12**, 57.

size-factors were favourable, the $\alpha/\alpha + \beta$ phase boundaries in many alloys of copper and silver could be roughly superimposed if the diagrams were drawn in terms of electron concentration instead of the more usual weight or atomic percentages of the elements. All this work led

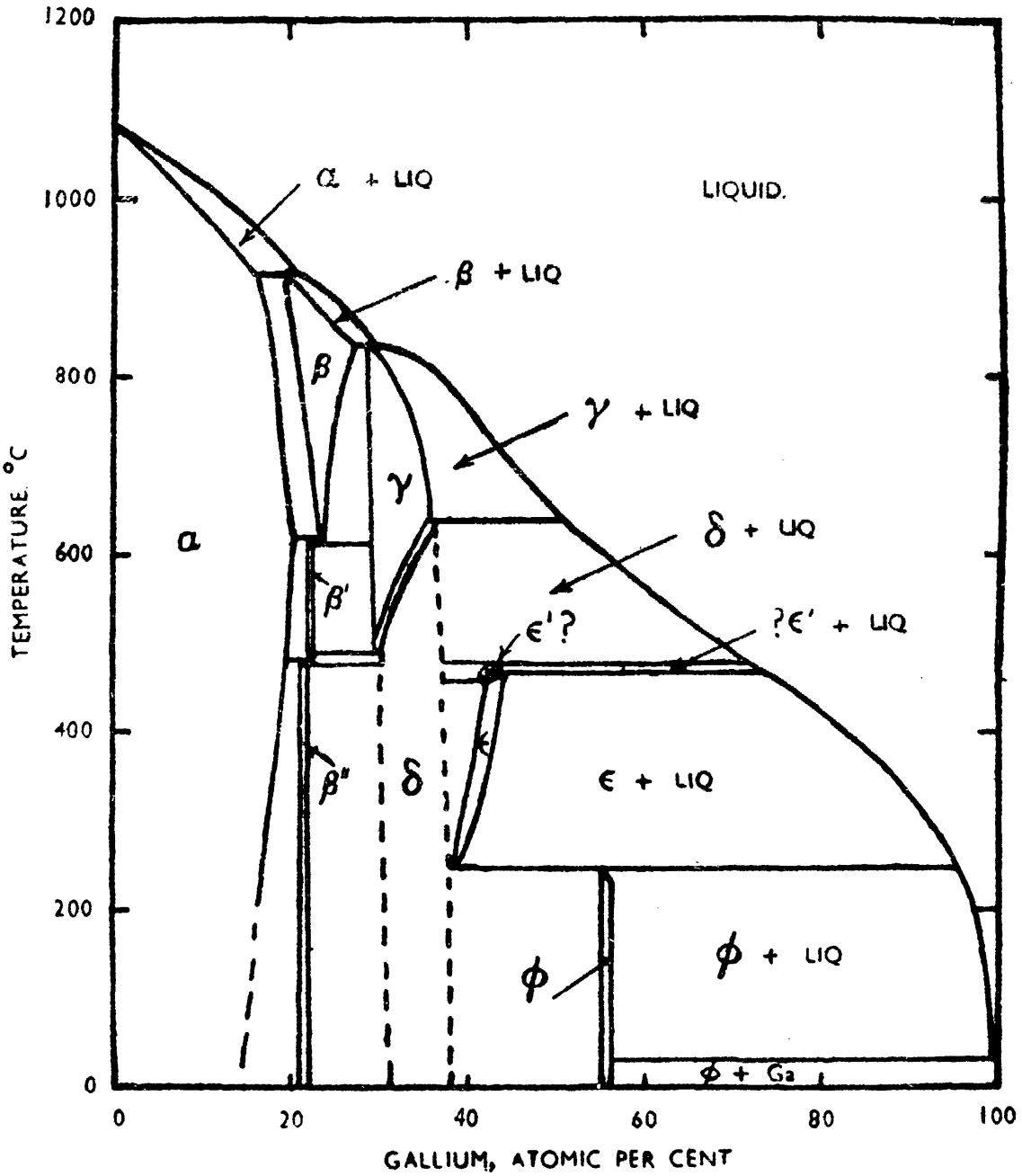


FIG. 45.—The Equilibrium Diagram of the System Copper-Gallium.

In this system the α-phase has the face-centred cubic structure of copper. The β-phase is body-centred cubic, whilst the δ-phase has a structure similar to that of the γ-brass. The β' and β'' phases are close-packed hexagonal. The copper-rich part of the diagram is known accurately, but the details of the remainder are not yet established, and in particular the transformations of the phases denoted ϵ, ϵ' are not understood. In order to secure clear reproduction, it has been necessary to exaggerate slightly the distances between some of the closely spaced lines, and the figure is not intended to be used for any purposes of measurement.

clearly to the conclusion that in some alloys the structures of the phases and the forms of the equilibrium diagrams were determined primarily by the electron concentration, and as suggested by J. D. Bernal, phases of this kind may conveniently be called *electron compounds*. In general,

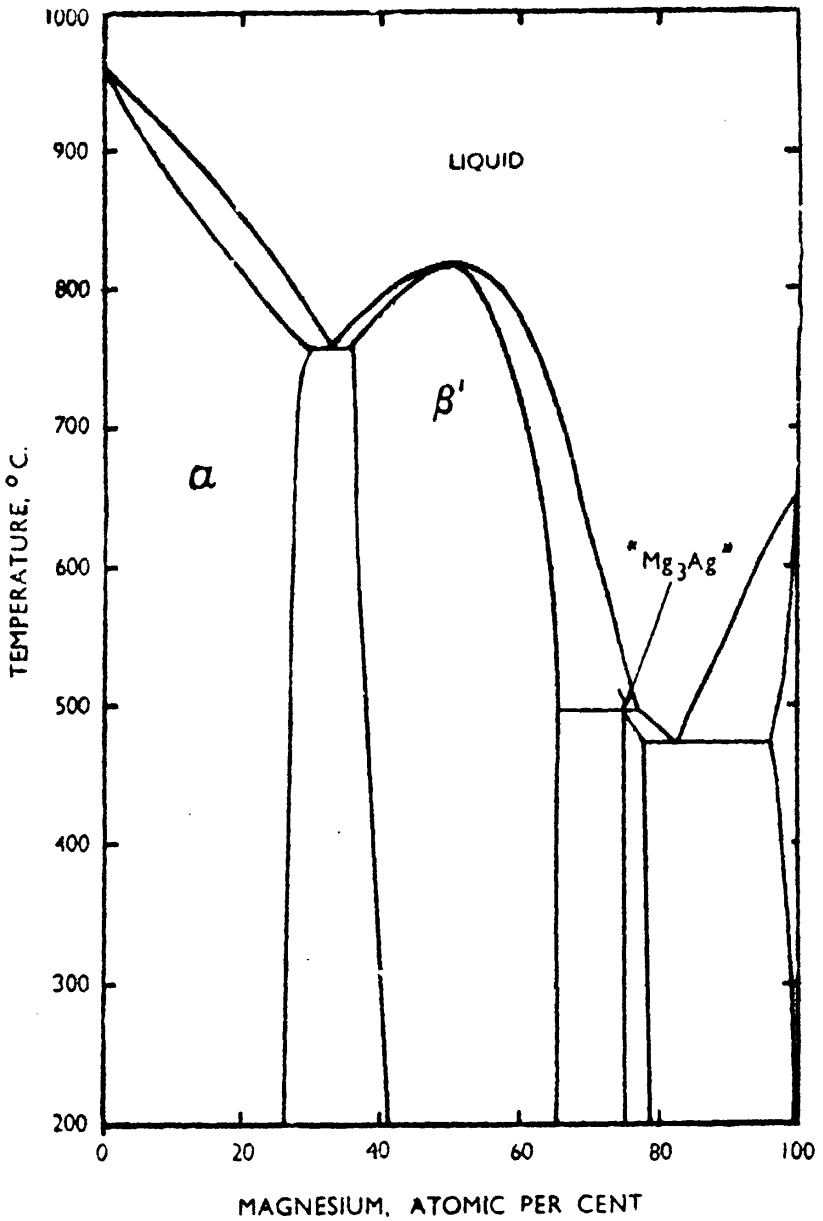


FIG. 46.—The Equilibrium Diagram of the System Silver–Magnesium.

The diagram is known accurately in the ranges 0–40 and 80–100 at.-% of magnesium. In the range 40–80 at.-% of magnesium the general form of the diagram is established conclusively, but the phase boundaries are not so accurate.

this class of compound is only formed when the size-factor is reasonably favourable, but the degree of toleration is greater than for primary solid solutions. Thus in the system copper–cadmium, the cadmium atom is so large that the primary solid solution in copper is very restricted, but a γ-phase of slightly varying composition is formed at a

composition near to Cu_5Cd_8. The very beautiful X-ray work of Bradley shows that although the general γ-type of structure is preserved, the detailed atomic arrangement in Cu_5Cd_8 is different from that in Cu_5Zn_8, where the size-factors are favourable. This clearly suggests that there may be a continuous transition from structures determined mainly by the electron concentration to those where the atomic diameters are the controlling factors. There are, however, many exceptions to these simple electron-concentration rules. Thus, in the system silver–lithium, a typical γ-brass structure is formed by an alloy whose composition is approximately Ag_3Li_{10}, although no combination of univalent elements can give an electron concentration of 21 : 13.

We shall describe in Part VI the theoretical explanation of these electron compounds, and for the moment we may merely note that in some alloys the electron concentration is clearly the essential factor in determining the structure of the alloy. Electron compounds may exist with ordered structures or superlattices, as in the low-temperature modification of β-brass, and also with what are usually called disordered or random structures as in the high-temperature form of β-brass. As in the case of primary solid solutions, there is very probably some kind of short-range order in what are usually classed as disordered electron compounds. The tendency for an electron compound to develop order (both long range and short range) increases with increasing electrochemical factor, and in this connection it is instructive to examine the equilibrium diagram of the system silver–magnesium (Fig. 46). In this case there is again a body-centred cubic phase in the equi-atomic region, but this now has a maximum freezing point at the equi-atomic composition, and possesses an ordered body-centred cubic structure in which the structure as a whole is body-centred cubic, but like atoms tend to avoid being closest neighbours, so that at the composition AgMg the alloy has the cæsium chloride structure shown in Fig. 47, where one kind of atom is situated at the centre and the other kind at the corners of the unit cubes.* When these two systems are compared, we see that silver is more electronegative than copper, and magnesium is more electropositive than zinc, so that the electrochemical factor is much greater in the system silver–magnesium than in the system copper–zinc, and it is this which accounts both for the greater stability of the ordered

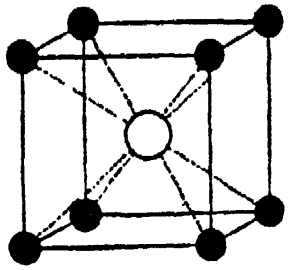


FIG. 47.—The CsCl structure.

* Alloys in the β-phase area of the silver–magnesium system with compositions other than 50 at.-% of magnesium cannot have a perfectly ordered structure, but they do have partly ordered structures in which like atoms tend to avoid being closest neighbours.

structure and the maximum freezing point of the β-magnesium–silver phase. It is uncertain whether definite MgAg molecules exist in the liquid alloy, but it is clear that increasing electrochemical factor has made the β-magnesium–silver phase acquire some of the characteristics (maximum freezing point and ordered structure) which are usually associated with definite chemical compounds.

Even in systems where a phase with an ordered structure is not

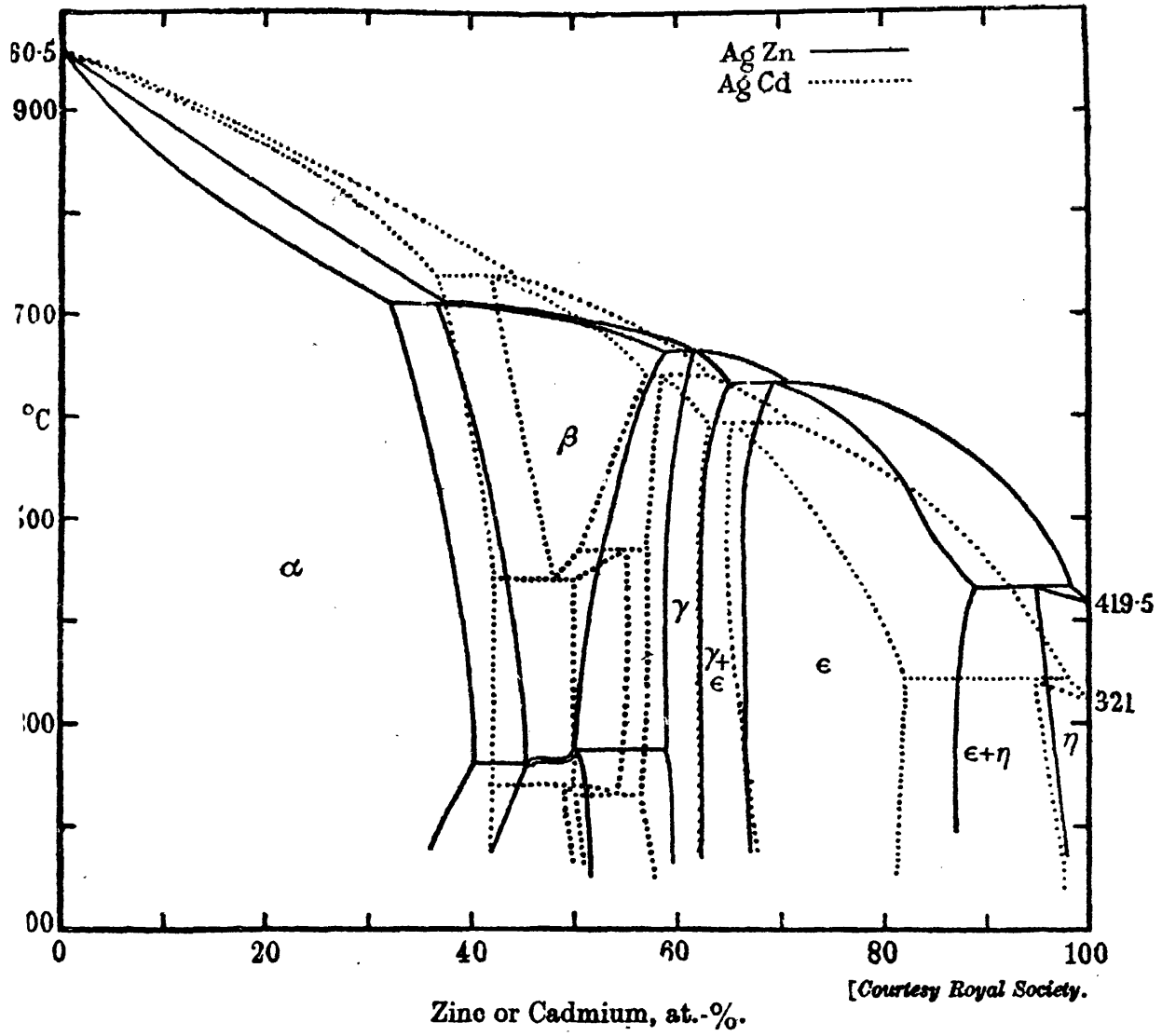


FIG. 48.—The Equilibrium Diagrams of the Systems Silver–Zinc and Silver–Cadmium.

formed, the effect of the electrochemical factor can sometimes be seen. Fig. 48 shows a comparison of the equilibrium diagrams of the systems silver–cadmium and silver–zinc. The high-temperature regions of these are quite analogous to that of the system copper–zinc, and in each case increasing percentage of the solute results in the face-centred cubic α-solid solution being followed by a two-phase region and a disordered body-centred-cubic β-phase. It will be noted that in the system silver–

zinc, the liquidus curve shows a much greater change in direction at the temperature of the (α + liquid $\rightleftharpoons$ β) peritectic horizontal than in the system silver–cadmium. Zinc is more electropositive than cadmium, and consequently the electrochemical factor is greater in the system silver–zinc, and the equilibrium diagram of the β-phase in the latter system is clearly beginning to acquire the characteristics of the silver–magnesium diagram, although the process has not been carried far enough to result in the production of a maximum in the liquidus curve. Other examples of this kind have been discovered * and it is important to realize that when the two constituents of an alloy differ considerably in electrochemical properties, the interatomic forces in the solid alloys are often partly of an ionic nature. In the elements copper, silver, and gold, the electronegative nature increases in the order :

$$\mathrm{Cu} < \mathrm{Ag} < \mathrm{Au}.$$

This means that in alloys with electropositive elements such as magnesium or zinc, the electrochemical factor increases in the order Cu < Ag < Au, whereas in alloys with electronegative elements such as arsenic, the electrochemical factor increases in the order Au < Ag < Cu. It follows also that in alloys of copper, silver, or gold, with a series of elements such as :

$$\mathrm{Zn} \rightarrow \mathrm{Ga} \rightarrow \mathrm{Ge} \rightarrow \mathrm{As} \rightarrow \mathrm{Se},$$

the element of Group IB begins by being the electronegative constituent of the alloy and finishes by being the electropositive constituent, and there is a point somewhere in the region of Group IVB where the electrochemical factor is very small.

Just as the electrochemical factor may result in an electron compound acquiring some of the characteristics of a polar compound, so there is no sharp boundary between electron compounds and compounds involving co-valent bonds, and there are undoubtedly cases where an electron compound involves atomic bonding of a partly co-valent nature. It will be realized, therefore, that the actual state of affairs in many alloy phases is very confused, since different types of interatomic cohesion may be superimposed, and may be modified by the difference in size of the atoms. In the case of the polar or ionic bond, we can obtain a reasonably simple picture of the process as the result of the attractions of opposite charges. The understanding of the co-valent bond is much more difficult, and we shall approach this subject by considering the general nature of the forces to be expected when two

* For a review of this work, see the paper by Hume-Rothery, Reynolds, and Raynor, *J. Inst. Metals*, 1940, **66**, 191.

atoms are brought into contact, and then the nature of the cohesive forces in some simple molecules. The metallurgical reader will appreciate that although these molecules are non-metallic, it is only by considering such comparatively simple structures that we can begin to understand the nature of the different kinds of force which are superimposed on one another in the crystals of metals.

Chapter XVI.—Atomic Attraction and the Nature of van der Waals Forces.

In the preceding chapters we have dealt with the characteristics of some of the main classes of substances, and we have now to consider the various processes which give rise to attraction between atoms, and hence to the formation of molecules, liquids, and solids. For this purpose we may consider first what happens when two atoms approach one another. In Part II we have seen that an atom is to be considered as consisting of a positively charged nucleus surrounded by a cloud of negative electricity, and for a first approximation we may assume that the electron clouds of two similar atoms are spherical. Although there is no sharp boundary to the electron cloud of an atom, the cloud density diminishes so rapidly beyond a certain distance that we are justified in

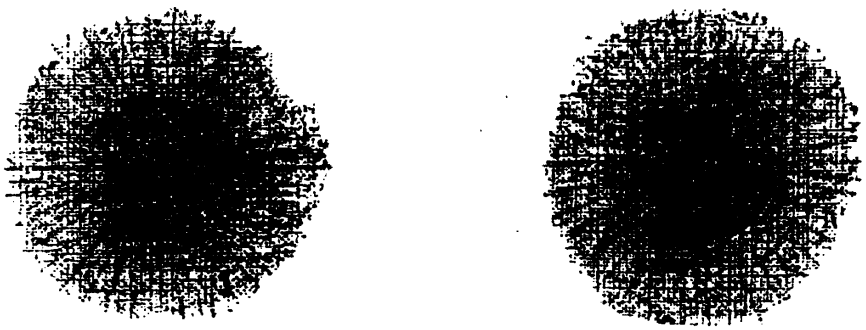


Fig. 49.

saying that some points are well outside the electron cloud of one atom, whilst others are inside.

We may now suppose that we have two atoms at a distance from one another which is greater than the extent of their electron clouds, as in Fig. 49. If the spherical electron clouds were static and undeformable, there would be no force between the two atoms. Actually, however, the electron clouds result from the motion of the various electrons, and although we can no longer follow the trajectories of these in detail, we must still regard the individual electrons as being in motion round their nuclei. We can see, therefore, that whilst an atom with a spherically symmetrical electron cloud will have no average electrical moment, or "dipole" moment, it will have a rapidly fluctuating dipole moment. Thus, in the sodium atom, the electron cloud of the 3*s* valency electron is spherically symmetrical, but at the instant when the

electron is to the left of the nucleus, there will be a preponderance of negative electricity on this side of the atom, and hence a temporary dipole will be formed with a +ve charge on the right, and a −ve charge on the left. When, therefore, two atoms approach one another, the rapidly fluctuating dipole moment in each atom will affect the motion of the electron in the other atom, and a lower energy (*i.e.*, an *attraction*) can be produced if the electrons in the two atoms move in sympathy with one another. This phenomenon, in which the electronic motions in two atoms harmonize or sympathize with one another, gives rise to the "van der Waals forces"; this name is used because it is these forces which are responsible for the attractive term in the well-known gas equation of van der Waals. These forces are also sometimes called "polarization forces," and they produce a potential energy proportional to $-1/r^6$, if the zero of potential energy is taken to be that of the atoms at an infinite distance apart.

When two atoms approach one another from a large distance, forces

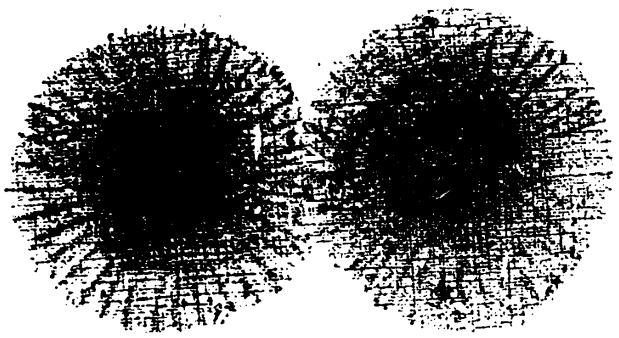


FIG. 50.

of the van der Waals type are always produced, and we may regard them as drawing the atoms together until the electron clouds overlap slightly as shown in Fig. 50. At this stage additional forces are introduced which, according to the nature of the atoms concerned, may produce either attraction or repulsion, quite apart from the van der Waals attraction. On the one hand, the fact that the electron clouds are overlapping slightly means that the outermost electrons of each atom are attracted by the nucleus of the other atom, and this produces an attraction between the two atoms. At the same time, the electron clouds repel one another, and as we shall see later (p. 134), wave mechanics indicates that this repulsion is particularly strong if the overlapping electron cloud is that of a complete group of 8 or 18 electrons.* As the atoms are drawn together the repulsion increases, until a stage is

* Or a group of 2 electrons in the first quantum shell.

reached at which the attraction and repulsion balance one another, and equilibrium results.

The van der Waals forces are the only long-range forces which exist between neutral atoms. In many substances as the atoms approach one another, these forces are rapidly outweighed by those of other kinds, but the van der Waals forces are always present, and in the case of the inert gases with complete groups of electrons in the outermost shell, they are the only attractive forces which can be produced. It is thus the van der Waals forces which serve to hold the atoms together in the solid and liquid states of the inert gases, and in these substances we are to regard the atoms as drawn together by the van der Waals forces until these are balanced by the repulsive forces caused by the overlapping clouds of the atoms. In the inert gases the van der Waals forces are weak because the octets of electrons are so stable that the electronic motion in any one atom can be only slightly disturbed by the motion of the electrons in adjacent atoms. It will be noted that the boiling points of the inert gases rise, *i.e.*, the interatomic bonding becomes stronger, with increasing atomic number; this is because the electron clouds become larger and are more easily deformed or polarized.

Forces of the van der Waals type are also responsible for the cohesion in liquid and solid hydrogen, nitrogen, and oxygen. Here the diatomic molecules are formed by simple co-valent bonds (electron sharing), and then the electrons in adjacent molecules move in sympathy or harmony with one another, and so give rise to van der Waals forces which draw the molecules together until the attraction is balanced by the repulsion due to the overlapping of the electron clouds of adjacent molecules. In the same way the cohesion between the iodine molecules in solid iodine (Fig. 32) is regarded as due to van der Waals forces, which are here clearly much more pronounced, since iodine is a solid at room temperatures. The cohesion between the chains of atoms in the structure of tellurium (Fig. 33) and between the double layers in antimony (Fig. 34) has also been ascribed to forces of the same nature.

Even when the main cohesion is due to forces of another kind, the van der Waals type of cohesion may still exist, and may exert an important influence. In the case of copper, for example, each atom has one valency electron outside a closed group of 18 electrons, and the general picture of the cohesion in solid copper is that the valency electrons are shared between adjacent atoms, and so serve to draw them together, until this attraction is balanced by the repulsion which results from the overlapping of the electron clouds of the ions. In this case, when we consider the motion of the valency electrons, we cannot regard these as completely independent of one another, because the electro-

static repulsion between two electrons prevents them from being in the same place at the same time. In this way the motion of the whole swarm of electrons is subject to what is called a *correlation effect*, in the sense that electrons tend to avoid each other. This correlation of motions affects the energy of the electrons, and these *correlation forces* are really an extension of the van der Waals forces to the case where the electrons are moving in the same region of space. In the same way, the electrons in the outer parts of an *ion* in solid copper are affected by the motion of the electrons in an adjacent ion, and if the two move in harmony there is a lowering of energy, and hence an attraction which is essentially of the van der Waals type.

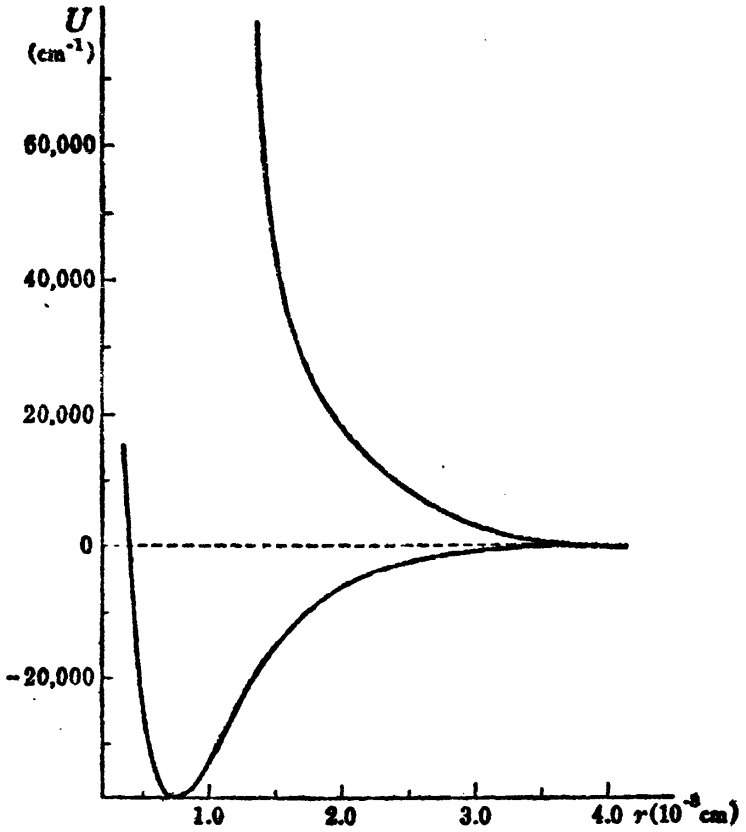
Chapter XVII.—The Interpretation of the Co-Valent Bond and the Nature of Exchange Forces.

In the above description we have seen how the van der Waals forces are to be understood as the result of a dynamic polarization of the electron cloud of one atom under the influence of adjacent atoms, and we have seen how this kind of attraction may exist in many types of substance, even where the main interatomic attraction is due to some other cause. We have now to consider how the simple co-valent bond is to be understood in terms of electron theory, and in particular why elements such as hydrogen, nitrogen, oxygen, and fluorine form stable diatomic molecules, whilst others such as helium or magnesium do not. The Lewis theory of the sharing of electrons so as to build up groups of 2, 8, or 18 electrons, is clearly satisfactory as a qualitative picture of the nature of valency, but it is entirely lacking in detail, and does not enable any quantitative estimation of properties such as heats of formation, interatomic distances, &c. We may begin by considering the interpretation of the diatomic hydrogen molecule, because this theory has been worked out in great detail, and the underlying principles illustrate many points which are also involved in the theory of metals.

In the theory of diatomic molecules, it is customary to use three methods of approach. These are really only different ways of describing the same phenomena, but each serves to emphasize some of the essential points. We may first use the method of *approach of widely separated atoms*, and may imagine that two hydrogen atoms in their normal states gradually approach one another. At any given distance apart, the wave functions of the system of two positive nuclei and two electrons yield acceptable solutions only for certain values of the energy, and, as in the problem of a free atom, these involve the introduction of quantum numbers. The quantum numbers of a molecule are complicated, and for the present purpose it is sufficient to say that just as in the case of a free atom, the quantum number m_l is a measure (in units of $h/2\pi$) of the component of the angular momentum in the direction of an applied field, so in the case of two atoms a quantum number λ is introduced, such that the component of angular momentum along the line joining the centres of the two atoms is equal to $h\lambda/2\pi$. It is then customary to denote states for which $\lambda = 0, 1, 2, 3 \ldots$ by the symbols σ, π, δ, ϕ. . . . An electron in a molecule has also a spin quantum number m_s which equals $\pm \frac{1}{2}$, and other quantum numbers which are more difficult to define. As in the free atom, the Pauli restriction principle

still applies to the electrons in a molecule, and only one electron can be in a given state as defined by all the quantum numbers, or alternatively only two electrons (of opposite spin) can occupy a given energy state as defined by the quantum numbers other than m_s.

When the hydrogen atoms are widely separated, their valency electrons are in the lowest or (1*s*) state of the individual atoms, and have the same energy. As the two atoms approach one another, each atom comes under the influence of the other, and the (1*s*) states split



[*Courtesy Prentice-Hall, Inc.*

FIG. 51.—Potential Curves of the Two Lowest States of the Hydrogen Molecule. The curves show how the internuclear distance affects the total energy of the molecule when the electrons are in the repulsive orbital (upper curve), and the attractive orbital (lower curve) respectively.

into two states of slightly different energies which are denoted σ_g 1*s* and σ_u 1*s*.* The total energy of the molecule is the sum of the Coulomb or electrostatic repulsion of the nuclei, and the energy of the electrons. If the atoms approach one another with their electrons in the (σ_u 1*s*) state, the energy of the molecule increases as shown in the upper curve of Fig. 51, and consequently electrons in this state will be repulsive. It is customary to call this electron state a repulsive " orbital," although,

* The subscripts *u* and *g* refer to the symmetry of the wave functions about the point midway between two atoms, and this need not concern us.

as in the case of free atoms, we cannot really follow the electron in detail round an orbit. If, however, the electrons are in the (σ_g 1*s*) state, the total energy of the molecule decreases as the atoms approach, and then passes through a minimum as shown in the lower curve of Fig. 51. Electrons in the (σ_g 1*s*) state will thus be attractive and will tend to form a stable molecule when the two atoms are at a distance apart corresponding with the minimum in the lower curve of Fig. 51. We have seen that each energy state can contain not more than two electrons which must be of opposite spin. Since each hydrogen atom contains one electron, we can see that if the two electrons have opposite spins, the pair of atoms possesses just sufficient electrons to fill the (σ_g 1*s*) orbital completely, and since this is an attractive orbital a stable H_2 molecule can be formed. In contrast to this, if two helium atoms approach one another, then although, as in hydrogen, their electrons are in (1*s*) states, there are now four electrons to be accommodated, and since the (σ_g 1*s*) orbital can accommodate only two electrons, it will be impossible to place all four electrons in this orbital, and all that can be done is to place two electrons in the attractive (σ_g 1*s*) and two in the repulsive (σ_u 1*s*) orbital. In this case there are equal numbers of attractive and repulsive electrons, and so a stable molecule is not formed. For the same reason we can see that if two hydrogen atoms have electrons with parallel spins, they cannot form a stable molecule, because Pauli's principle allows only one electron of a given spin to be in a given state, and so if the spins of the two electrons are parallel, only one can be in the (σ_g 1*s*) attractive orbital, and the other will have to be in the (σ_u 1*s*) repulsive orbital, and there will again be equal numbers of attractive and repulsive electrons, and consequently no stable molecule. We see, therefore, that the formation of a stable H_2 molecule on the one hand and the non-existence of a stable He_2 molecule on the other, is the result of the following set of circumstances :

(1) As the atoms approach one another, the single 1*s* level splits into two levels, and one of these is characterized by giving a minimum in the curve connecting the total energy of the molecule with the interatomic distance, whilst the other corresponds with repulsion.

(2) In the case of H_2, there are only 2 electrons to be accommodated, and if these have opposite spins they can both occupy the attractive orbital.

(3) In the case of helium, there are 4 electrons to be accommodated for every two atoms, and hence by Pauli's Principle only two

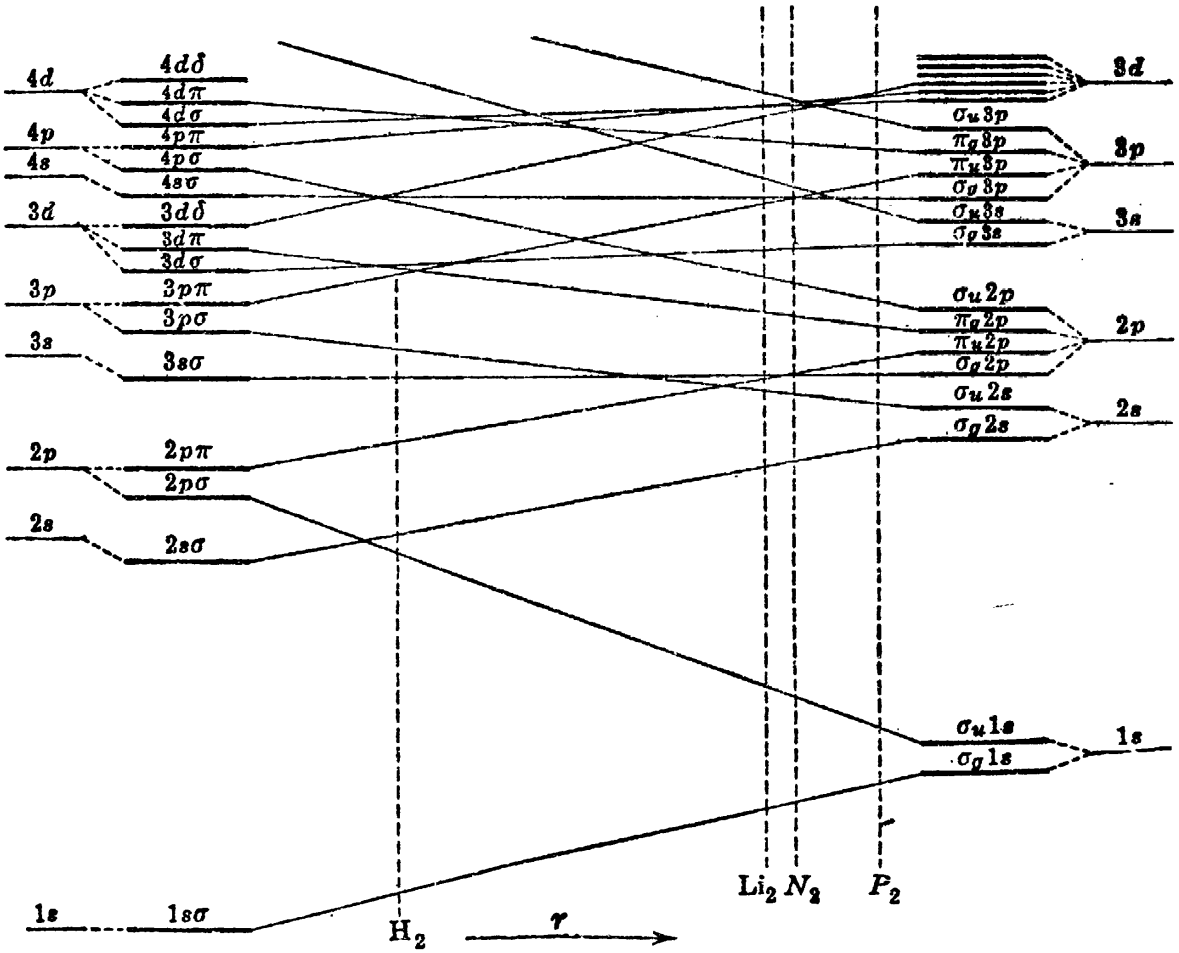
of these can enter the attractive orbital, while the other two enter the repulsive orbital, and it can be shown that the repulsion is the stronger.

It is to be noted that the above splitting of the (1*s*) level as two atoms of hydrogen approach one another is quite analogous to the broadening of the energy levels of valency electrons in solid metals which is revealed by soft X-ray spectroscopy (p. 87). In the hydrogen molecule there are only two atoms, and the (1*s*) level splits into two sub-levels only. In a metal crystal the number of atoms is of the order of 10^{23} per c.c., and the splitting of the level is correspondingly fine, but the essential process is the same.

It will be seen from Fig. 51 that the total energy of the molecule when the electrons are in the attractive orbital gives a curve with a minimum, and consequently when the electron is in this state, it is possible for the molecule to have vibrational energy corresponding to vibrations of the atoms about the line joining their centres, and these vibrational states are stable provided that the energy is not sufficient to make the system jump out of the potential valley. In this way the single energy value of the electronic state may be accompanied by a number of vibrational energies, and corresponding "vibration spectra" are obtained. This serves to indicate a very general principle that any system where the curve connecting energy with interatomic distance shows a minimum, may possess vibrational energy up to a certain limit.

The second way of looking at the formation of a diatomic molecule is to imagine the two atoms to approach each other so closely that they coalesce and form what is called a "united atom." The united atom may then be regarded as gradually separating into two atoms, and it can be shown that the first stages of this separation affect the energy levels of the united atom in the same way as the application of a strong electric field. The interest of this method is that when combined with Pauli's Principle, it gives an indication of the way in which the energy levels of the diatomic molecule are related to those of the free atoms. We may suppose, for example, that two lithium atoms, each containing 3 electrons, unite to form a carbon atom containing 6 electrons. In a free lithium atom, the electronic configuration is $(1s)^2(2s)^1$, but since the (2*s*) level can contain only 2 electrons, the united atom will have some of its electrons in (2*p*) states. In this way it is possible to draw a diagram such as that of Fig. 52, in which the right-hand side shows the electron levels of the free atoms and the left-hand side the levels of the united atom, and the connecting lines show how the states of the one

pass into those of the other as the interatomic distance is varied. If, on passing from right to left, a line slopes upwards, it implies that the energy increases as the distance between the two atoms decreases, and this corresponds to a repulsive or anti-bonding orbital; whilst if



[*Courtesy Prentice-Hall, Inc.*

FIG. 52.—Correlation of Electronic Orbitals in a Two-Centre System for Equal Nuclear Charges.

To the extreme left and the extreme right are given the orbitals in the united and separated atoms, respectively, and, beside them, those in the molecule for very small and very large nuclear separations, respectively. The region between corresponds to intermediate nuclear separations. The vertical broken lines give the approximate positions in the diagram that correspond to the molecules indicated. It should be noticed that the scale of r is by no means linear, but becomes rapidly smaller on the right-hand side. Owing to this change of scale, the straight connecting lines between right and left do not correspond to a linear energy change with r, but to one that is closer to reality, even though it is an admittedly poor approximation.

the line slopes downwards it implies that the orbital is attractive or bonding. Pauli's Principle indicates that each σ sub-group of the molecule can contain only 2 electrons, and each π or δ sub-group can contain only 4 electrons.

If Fig. 52 is applied to the case of two hydrogen atoms, it will be seen that the (1*s*) level is shown as splitting into the (σ_u 1*s*) and (σ_g 1*s*) levels, and the second of these slopes downwards, and hence indicates a bonding orbital, which can contain the two electrons. The line for the (σ_u 1*s*) level slopes upwards, and thus indicates an anti-bonding orbital, and hence, as explained above, a combination of two helium atoms has two electrons in bonding, and two in anti-bonding orbitals, and there is no stable molecule. In the case of lithium there are six electrons to be accommodated in a diatomic molecule. Of these the two *K* electrons of each atom enter the (σ_u 1*s*) and (σ_g 1*s*) orbitals of the pair of atoms, and these may be regarded as taking no part in the bonding process, since the *K* electrons occupy the inner part of the atom and so are only affected appreciably when the atoms are very close together, and in any case they only give rise to equal numbers of bonding and anti-bonding orbitals. The (2*s*) valency electrons of the free atoms can enter the (σ_g 2*s*) orbital of the pair of atoms, and since the line for this slopes down from right to left in Fig. 52, a stable Li_2 molecule is formed. Fig. 52 is purely diagrammatic: the horizontal scale of distances is not uniform, and if it were uniform, the lines joining the various levels would no longer be straight. Further, the relative position of the energy levels of the individual atoms and the united atom will vary according to the element concerned. But when used in conjunction with Pauli's Principle, diagrams such as that of Fig. 52 are extremely useful in showing how, when two atoms approach one another, bonding and/or anti-bonding orbitals may be formed. It will be noted further that for relatively large distances of approach, the splitting of the groups shown in Fig. 52 result in the groups of sub-levels derived from the 1*s*, 2*s*, 2*p*, &c., levels of the free atoms remaining separated from one another, although at closer distances of approach they overlap or intersect. This is entirely analogous to the overlapping of the energy bands in metals referred to on p. 88, and Fig. 52 is really only showing for a diatomic molecule what Fig. 27 shows for the immense molecule formed by the crystal of a metal. Fig. 52 refers to the interaction between two like atoms, but analogous diagrams can also be drawn for the processes which occur when two unlike atoms approach one another, and in principle similar diagrams could be drawn for more complicated systems.

The third method of regarding the formation of the hydrogen molecule is the most instructive from our point of view, and consists in assuming that the centres of the two nuclei are at a given distance apart, and then calculating the possible wave functions for the system of two electrons in the field of the two nuclei at this distance. As explained

above, the possible energy states will then involve the introduction of quantum numbers, and, just as in the case of a free atom, we must interpret $\Psi\Psi^*$ as a measure of the electron density at the element of volume concerned. We shall not deal here with any of the details of the calculation, but it is necessary to explain the way in which what are called the " exchange forces " come into being. We may suppose that we denote the two hydrogen atoms by the letters A and B, and the two electrons by the numbers 1 and 2, and that at a particular instant electron No. 1 is moving round atom A and electron No. 2 round atom B. Then, since electrons are indistinguishable, an exactly similar system would exist if the electrons interchanged so that electron No. 2 was near atom A and No. 1 near atom B. It is now a general principle of this kind of calculation that if a system can exist in alternative configurations, the lowest energy of the system is not that of the wave function of either configuration alone, but is formed by the superposition of the two wave functions. If we use a symbol such as $\Psi_{1A}\Psi_{2B}$ to denote the wave function when electron No. 1 is with atom A and No. 2 with atom B, then as the atoms approach one another the wave functions are of the form

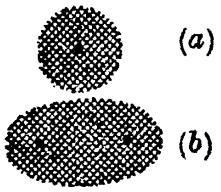
$$\Psi_{1A}\Psi_{2B} + \Psi_{1B}\Psi_{2A}$$

and

$$\Psi_{1A}\Psi_{2B} - \Psi_{1B}\Psi_{2A}.$$

Of these only the first gives a minimum in the curve connecting the total energy of the molecule and the distance between the atoms, and so corresponds to attraction. This is a possible state of the system only if the electrons have opposite spins; it is in fact the state which we have called (σ_g 1s) in Fig. 52. This superposition of wave functions may be interpreted as an oscillation or interchange between the two configurations. When the atoms are comparatively far apart, the interchange is slight, and we may regard a given electron as moving round one particular atom for a comparatively long time, and then passing over to the other atom. As the atoms approach each other the interchange of electrons becomes more rapid, and at the equilibrium distance between the two hydrogen atoms in the H_2 molecule (0·74 A.) the frequency of the interchange is of the order of 10^{18} per sec. This is very much more rapid than the frequencies of the vibration of the relatively heavy atoms, which are of the order of 10^{12} per sec. The interchange between the two configurations is thus so rapid that for most purposes we are no longer justified in thinking of the electrons as changing from one atom to another, but have rather to think of the average electron distribution of the system as a whole. As we shall see in the next section, this interchange or resonance between two alternative configurations has the effect of lowering the energy of the system, and of reducing the

interatomic distances, and these effects are greater as the energies of the two configurations are more nearly equal. In the hydrogen molecule the interchange of electrons between the two atoms produces systems which are indistinguishable, and hence the conditions for strong resonance bonding are present. The electrons in the H_2 molecule must therefore no longer be regarded as associated with individual atoms, but rather as forming a new configuration in which they are associated with the system as a whole, and this new configuration may have properties which are different from those of the configurations between which resonance occurs. The electron density in the H_2 molecule can be represented by diagrams analogous to those used for free atoms, and Fig. 53 shows the general form of the electron-cloud pattern of the (σ_g 1*s*) state in sections perpendicular to and passing through the line joining the centres of the two atoms. Higher energy states of the H_2



[*Courtesy Prentice-Hall, Inc.*

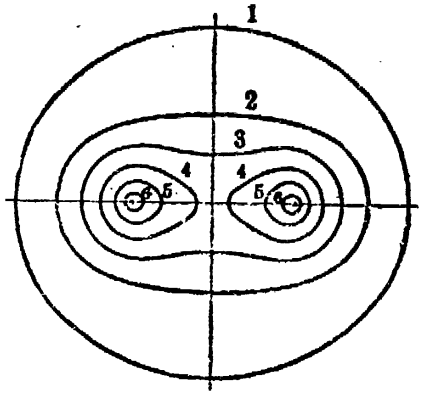
FIG. 53.—Diagrammatic Representations of H_2 Molecule.

The electron cloud is axially symmetrical about the line joining the two nuclei, and Fig. 53(*a*) represents a cross-section perpendicular to this axis, whilst (*b*) represents a cross-section containing the line which joins the nuclei. The details of the electron-cloud density can be obtained from Fig. 54.

molecule can also be formed, and these possess nodal surfaces or planes analogous to those in the higher states of the free atom.

Fig. 54 shows the electron-cloud density in a section through the two nuclei. The contour lines are lines of constant electron density, and it will be seen that these tend to crowd together in the space between the two atoms, and this is an illustration of a very general principle. In general any system of atoms and electrons, whether a molecule or a crystal, has a number of possible electronic energy states, and Pauli's Principle means that any one state can be occupied by only two electrons (of opposite spins). In nearly all cases—ferromagnetism is an exception—this means that electrons of opposite spins can pack together more closely, and with lower energy than electrons of the same spin. We can illustrate this readily for the case of a free atom. In the atom of neon, for example, the normal electronic configuration is $(1s)^2(2s)^2(2p)^6$. Here the $(1s)^2$, $(2s)^2$, and $(2p)^6$ groups contain pairs of electrons with opposite spins. If all the electrons had the same spin, Pauli's Principle would mean that an *s* sub-group could only contain

one electron, and a p sub-group three electrons, and the lowest possible energy state of a hypothetical atom in which ten electrons all had the same spin would be $(1s)^1(2s)^1(2p)^3(3s)^1(3p)^3(4s)^1$. In this case the energy would be greater than that of the normal neon atom, and the electron cloud would occupy a much larger region of space. It must be emphasized that it is not a question of spinning electrons producing fields which repel one another, but rather that Pauli's Principle prohibits electrons of the same spin from occupying the same state, and so compels an assembly of electrons of like spin to occupy higher energy states than electrons of opposite spins. In most problems this is equivalent to



[*Courtesy Prentice-Hall, Inc.*

FIG. 54.

In this diagram the electron-cloud density in the space surrounding a hydrogen H_2 molecule is shown for a section passing through the two nuclei; the distance between the nuclei is 0·74 A. The curves are curves of equal probability density, and the numbers give the relative values of the density. It will be seen that the high electron density (contours 3, 4, 5, 6) tends to be concentrated in the region between the nuclei. The electron cloud is axially symmetrical about the line joining the nuclei, so that the energy contours in sections perpendicular to this line are circles whose spacing can be determined by drawing vertical lines in Fig. 54, and seeing where these intersect the different contours. Fig. 54 thus shows the detail inside Fig. 53(b), whilst Fig. 53(a) could be elaborated into a series of diagrams with circular contours depending on the position of the section across the internuclear axis.

saying that electrons in pairs of opposite spin can occupy a given volume with a lower energy, or alternatively for a given energy can occupy a smaller volume than an assembly of electrons of parallel spins.

In the previous section we have seen that as atoms approach one another to form a metal crystal, the van der Waals forces pass into the more extreme form of the correlation forces, in which their similar charges prevent two electrons from occupying the same place at the same time. Apart from this simple correlation effect, the exchange principles described above imply that electrons with parallel spin tend to avoid one another on account of Pauli's Principle. In co-valent bonds the theory indicates that electrons of opposite spin tend to crowd

together more closely than they would do if the principles of wave mechanics did not operate, but this effect is not found in simple metallic bonding, such as that in the crystals of the alkali metals. As explained in Chapter XV many alloy structures involve bonds which are partly metallic and partly co-valent, and the more pronounced the co-valent nature of the binding, the greater is the tendency for electrons of opposite spin to crowd together in the direction of the bond, whilst electrons of parallel spin always tend to avoid one another on account of Pauli's Principle. These exchange effects have to be taken into account in attempting to calculate the behaviour of electrons in the periodic field of a crystal, and the mathematical treatment becomes correspondingly complicated.

The exchange effects are also important in connection with the repulsion produced when the electron clouds of two ions overlap. In the above description we have frequently referred to atoms or ions being drawn together until the attractive forces are balanced by the repulsion caused by the overlapping of the electron clouds of the ions. If the electron clouds were spherical, static and undeformable, repulsion would occur only when the atoms were so close together that the nucleus of one was within the electron cloud of the other. If, however, we are dealing with completed groups of 2 (the helium configuration), 8, or 18 electrons, the ion contains only completely filled shells, and the exchange effects imply that comparatively slight overlapping of the electron clouds must result in an enormously increased energy. This is because when two ions approach so closely that their electron clouds overlap and they begin to form a joint system, the energy levels of the original ions split up to form groups of levels as in Fig. 52. If the ions contain completed groups of 8 or 18 electrons, the Pauli Principle prevents the electrons from redistributing themselves so as to obtain a lower energy as the atoms approach, and the energies of the states whose electrons give rise to the outer part of the ions increase rapidly as the atoms approach, *i.e.*, they correspond to lines sloping upwards from right to left in Fig. 52. In some cases this kind of repulsion may be superimposed on an attraction of the van der Waals type. In a crystal of copper, for example, the valency electrons are to be regarded as drawing the atoms together, and the electrons in the outermost parts of the ions then move in harmony with one another, and so give rise to additional attractive forces of a van der Waals type. But at the same time as the electron clouds of the ions begin to overlap, the repulsion resulting from the effects of the Pauli Principle comes into play. In a sense, therefore, we may say that the electrons in the outermost parts of the ions of copper, silver, and gold are responsible both for increased attraction, and hence

higher melting points, and increased repulsion, and hence lower compressibilities.

The normal co-valent bond, as explained above, always involves two electrons of opposite spins, but in some cases one-electron bonds can also be formed. Thus the hydrogen molecule ion, H_2+ contains two atoms bound together by one electron, and this electron is shared between the two nuclei and binds them together. We shall not deal here with the details of this kind of bonding, but its existence should be noted in connection with the theories of resonance which are described later.

Chapter XVIII.—Directed Valencies.

In the preceding section we have described some of the electronic processes which result in the formation of the H_2 hydrogen molecule. These processes involve the (1*s*) electrons of the free hydrogen atoms, and as the electron cloud patterns of these are spherically symmetrical, there is no reason to expect any directional effects. We have seen (p. 53) that on passing along the series of elements preceding an inert gas, the electronic structure builds up in such a way that first of all the $(ns)^2$ sub-group is built up with two electrons of opposite spin, and then as the electrons enter the $(np)^6$ sub-group, they take up parallel spins as

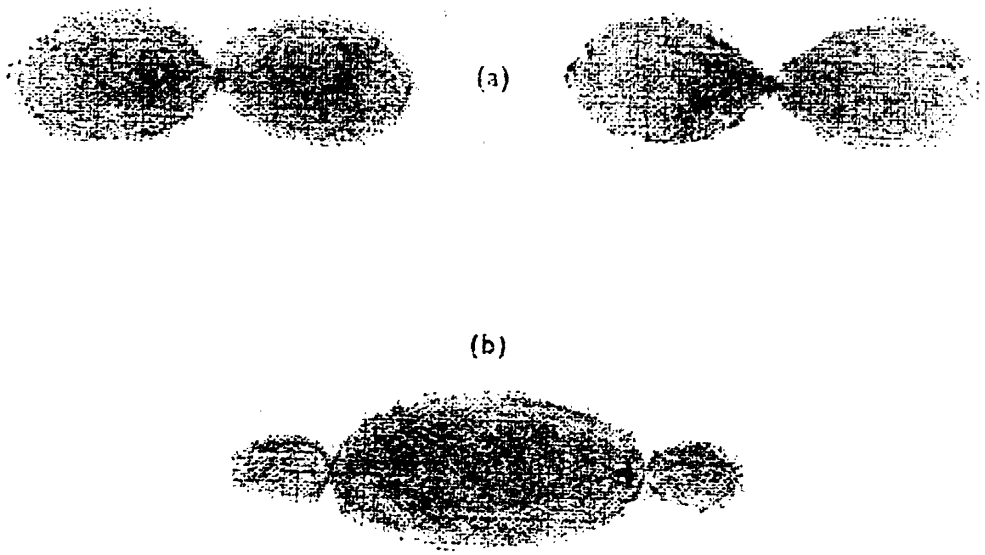


Fig. 55.

(*a*) Half-filled *p* orbitals of the free atoms approaching one another. Each *p* orbital contains one electron, and these must have opposite spins if bonding is to occur.

(*b*) The same two atoms after bonding has occurred, and the electron cloud is drawn between two atoms. The bond is formed by two electrons of opposite spin.

long as this is possible. Since the $(np)^6$ sub-group contains three orbitals, each of which can hold two electrons (of opposite spin), this implies that a normal atom of Group VB has an electron in each *p* orbital, and is spherically symmetrical. In Group VIB each atom in its normal state has one *p* orbital completely occupied by two electrons of opposite spins, whilst the other two *p* orbitals contain one electron each. Similarly, in Group VIIB the atom in its normal state has two of its *p* orbitals completely filled, whilst the third contains one electron only.

We have already seen that a co-valent bond is formed by two electrons

of opposite spin, and we can understand, therefore, why a fully occupied orbital does not take part in normal bond formation, since its two electrons have already paired their spins. The co-valent bonds of these elements are therefore formed by electrons in the orbitals which contain only one electron, or in other words by the unpaired electrons of the free atom.

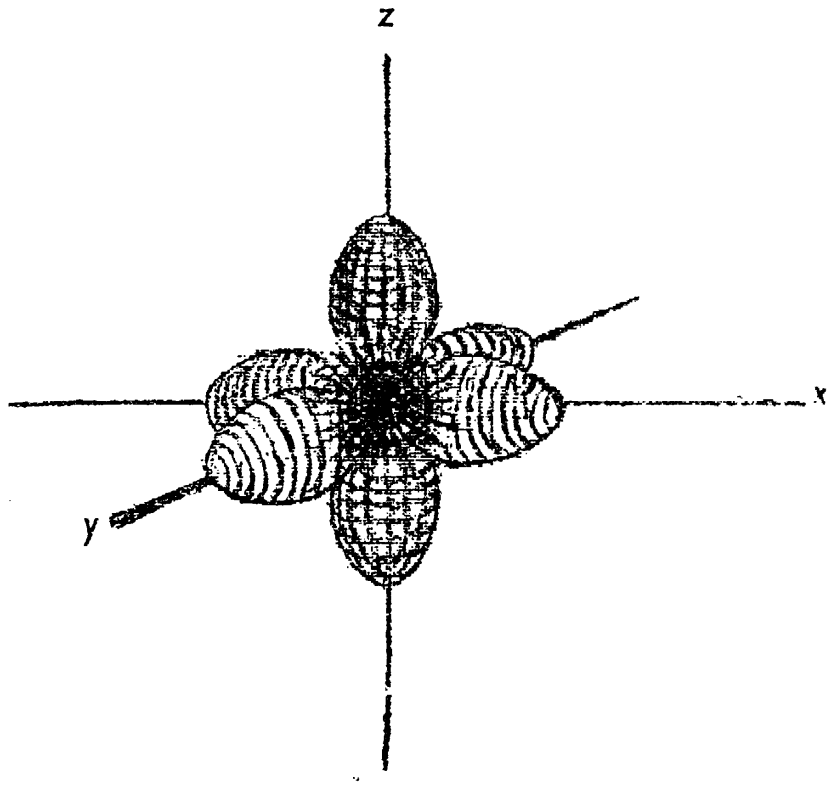


FIG. 56.—Diagrammatic Representation of an Atom of Selenium.

The inner electrons are shown as a dark area. The $(4s)^2$ sub-group is not shown; its electron cloud is spherically symmetrical with 3 spherical nodes. The $4p$ orbital extending along the z axis is shown with double markings and contains two electrons of opposite spins. The other two p orbitals, which contain one electron each, extend in the direction of the x and y axes respectively, and are shown with single markings. The figure is highly diagrammatic and is shown to emphasize the directions of the orbitals. In the actual atom the total electron-cloud density is the sum of the densities of the three orbitals. In the free atoms of N, P, As, Sb, and Bi each p orbital contains one electron, and the total electron-cloud density is spherically symmetrical as explained on p. 78. In selenium, where one p orbital contains two electrons, the electron density will be greater in the direction of this orbital, *i.e.*, greater in the direction of the z axis in Fig. 56.

When a bond is formed, the electron cloud is drawn into the space between the two atoms, so that if the electron cloud patterns of p states in two atoms are as shown in Fig. 55(a), the cloud pattern after the bond is formed is more like Fig. 55(b).

In Part II we have seen that the electron clouds of the three p orbitals are mutually perpendicular, and we might therefore represent a normal atom of selenium by a diagram such as that of Fig. 56. Here

the electron clouds of the inner electrons and of the two (4*s*) electrons are shown as a shaded region, and the electron cloud of the fully occupied (4*p*) orbital is shown with cross hatching, and since this contains two electrons of opposite spin, it does not give rise to bonding. The two remaining (4*p*) electron clouds contain one electron each, and as electron clouds are perpendicular, it is easy to see how a series of these atoms unite, as shown in Fig. 57, to form the spiral chain of the selenium structure shown in Fig. 35; the actual angles in the structures of selen-

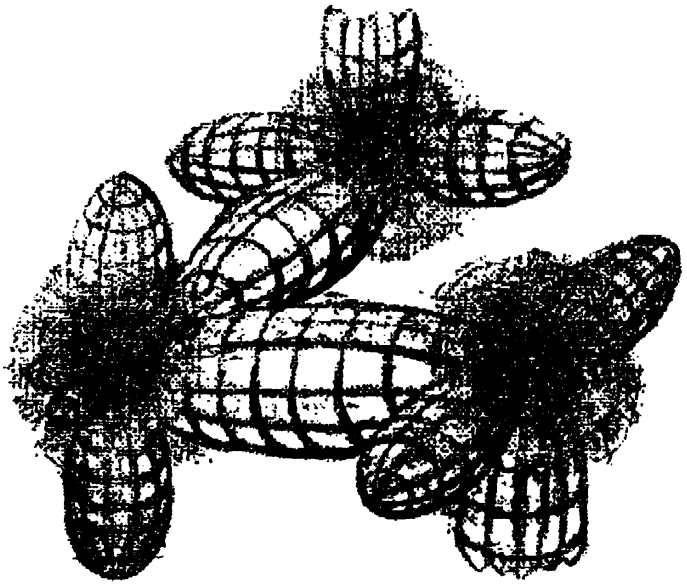


FIG. 57.

This figure shows diagrammatically how the selenium atoms of Fig. 56 unite to form the spiral chains in the crystal of selenium shown in Fig. 35. The inner electrons of each atom are shown by a shaded region. The two unpaired *p* orbitals of the valency electron of each selenium atom coalesce with those of adjacent atoms to form completely filled orbitals, each containing two electrons of opposite spin.

The electron clouds of the shared electrons in each co-valent bond are, of course, not really bounded by sharp surfaces but are diffuse. The surfaces are drawn as shown to illustrate the axial symmetry of the electron cloud about the direction of the bond, and about four-fifths of the charge would be contained within the volumes shown.

ium and tellurium are 105° and 102°, so that the exact right angles have been slightly distorted. Similarly, in the Group V elements, where the free atoms have three unpaired *p* electrons, we can see how these will tend to bind together to form the antimony structure of Fig. 34. In this case the angles between the bonds are much more nearly right angles, being 97°, 96°, and 94° for arsenic, antimony, and bismuth respectively. We can thus see that the wave-mechanical picture of mutually perpendicular *p* orbitals gives a very satisfactory account of the crystal structures of arsenic, antimony, bismuth, selenium, and tellurium. It is

also to be noted that the co-valent bonds formed by p orbitals are stronger than those formed by s orbitals.

The electron configuration of the normal state of the carbon atom is $(1s)^2(2s)^2(2p)^2$, in which the two $(2s)$ electrons form a pair with opposite spins, whilst the two $(2p)$ electrons are unpaired. In this state the carbon atom would have a co-valency of two, since there are only two unpaired electrons. The normal co-valency of four which is shown by the carbon atom is the result of the fact that the electron cloud of the $(2s)^2$ group in the free atom is still near the surface of the atom. In the free atom the configuration $(1s)^2(2s)^2(2p)^2$ gives the lowest possible energy, but in an assembly of atoms, more stable bonds can be formed by an electronic re-arrangement which may be regarded as giving rise to bonds derived from the $(1s)^2(2s)^1(2p)^3$ state of the free atom. In this state, the free atom has four unpaired electrons, and can consequently give rise to four co-valent bonds. It might at first be thought that these would consist of three mutually perpendicular bonds derived from the three $2p$ states, together with a fourth bond at some other angle, resulting from the $2s$ state. Actually this is not so, and the process of hybridization (p. 88) occurs, as a result of which the $2s$ and $2p$ states combine to form a set of hybrid orbitals, and it can be shown that these are directed tetrahedrally; * they are very strong bonds, in the sense that there is a high concentration of electrons in the region between two atoms which are close neighbours. This, of course, is only possible if the two electrons in a bond have opposite spins, and all co-valent bonds of this type involve two electrons of opposite spin. The formation of co-valent bonds of this type is not confined to cases where the atoms are similar, and in this way the wave-mechanical theory is able to explain the tetrahedral structure of crystals such as those of silicon, germanium, and grey tin, and also the wurzite and zinc-blende structures, where the tetrahedral arrangement is again found provided that the two kinds of atom contain on the average 4 valency electrons per atom.

The co-valent bonds in structures such as those of the diamond involve exchange forces similar to those described above (p. 131) for the H_2 molecule, and we have again to imagine the electrons concerned as undergoing a rapid interchange between two atoms. Since each atom has four neighbours, the valency electrons undergo a continual interchange between the different atoms in the crystal, and we must not regard a given pair of electrons as permanently associated with a given bond. The whole swarm of electrons is continually circulating through

* When hybridization takes place in carbon, the tetrahedral angles are not necessarily exactly equal, and may in some cases (*e.g.*, CH_3Cl) be a few degrees different from the angles of a regular tetrahedral arrangement.

the crystal, although the electron cloud density round an atom is very much greater in the direction of the four co-valent bonds joining the atom concerned to its four neighbours. Claims have been made to detect this concentration of electrons in the directions of the co-valent bonds, by means of refined X-ray crystal analysis. At first sight it might be imagined that this continual circulation of the swarm of electrons through the crystal would make the latter a conductor, but as we shall see later (Part V) this difficulty has been resolved satisfactorily by the theory of Brillouin zones. Here we may content ourselves with saying that electrical conductivity implies the possibility of a resultant flow of electrons in one direction, and this necessitates the existence of unoccupied electron states into which the electrons may be transferred by the action of an external field. If all the electronic states of a system are occupied, the application of an external field * can produce no alteration in the velocity distribution of the electrons as a whole, and it can be shown that in the case of the diamond the valency electrons completely fill one band of energy states, and that a very high external E.M.F. is necessary to excite electrons into the electron states of the next band. In this way the concept of a swarm of electrons in continual motion through the crystal can be reconciled with the absence of a resultant flow in any direction, and hence with the properties of an insulator.

Hybridization between s and p orbitals cannot give rise to more than four bonding orbitals to each atom, and consequently the highest co-valency of the elements in the first two Short Periods is usually four, since more than this number of bonds would necessitate the use of the d orbitals and these are of considerably higher energy. We have, however, seen that in the first Long Period, the $3d$ and $4s$ states of the free atoms have nearly the same energies, and in compound molecules of these elements hybridization can occur between the $3d$, $4s$, and $4p$ orbitals with the production of very stable bonding orbitals, which may assume different configurations. Thus, in stable complex ions such as $Co(NH_3)_6^{+++}$, the six NH_3 groups are situated at the corners of a regular octahedron, and are bound to the central cobalt atom by hybrid s, p, d orbitals. In the $(PdCl_4)^{--}$ ion the four chlorine atoms are arranged at the corners of a square. Up to the present, directed bonds of this kind have not been of much interest in connection with the structure of metals and alloys, but according to Pauling the fact that hybridization may occur between the ns, np and $(n-1)d$ orbitals of transitional elements † is of great interest in connection with the

* We are here ignoring the effects of very strong fields which break down insulators.

† Here n is the quantum number of the valency electrons.

cohesive forces in the crystals of these metals. The *s*, *p*, and *d* groups contain 1, 3, and 5 orbitals respectively, so that as many as nine orbitals per atom are available for bond formation in the transition elements, and although the evidence suggests that in metals these are not all used, the high melting points and strong cohesion of the crystals of transition metals are connected with the larger number of orbitals from which bonds may be formed.

Chapter XIX.—Resonance Bonding and the Metallic Linkage.

In the description of the hydrogen molecule we have seen that it is necessary to take into account the fact that two configurations of identical energy are produced if an arrangement with electrons No. 1 and 2 near nuclei A and B respectively changes to one with electron No. 1 near to nucleus B, and electron No. 2 near to nucleus A. We have seen further that this produces a rapid interchange or resonance between the two electronic configurations, with a resulting lowering of energy and decrease in the interatomic distance. This is an illustration of a general principle which may be summarized by saying that if a molecule can exist in more than one structure, the most stable state does not correspond to the wave function of any one structure, but to the superposition of wave functions of the different structures. If, for example, Ψ_1, Ψ_2, Ψ_3 . . . are the wave functions for a given molecule in a number of structures 1, 2, 3 . . . ., then a general function of the form

$$\Psi = a\Psi_1 + b\Psi_2 + c\Psi_3 \ldots$$

where a, b, c . . . are arbitrary numerical coefficients, is a possible wave function of the system, and the lowest possible energy of the system will correspond to a definite ratio $a : b : c$. . . . If one structure, say Ψ_2, is relatively much more stable than the others, then the ratios $a : b$, $c : b$, . . . will be small, and the most stable state will resemble that of Ψ_2 more closely than any other state, although there will be a slight mixture or superposition of the other states, which may be interpreted by saying that the molecule resonates or oscillates with high frequency between the different states, whilst spending most of its time in a condition closely resembling that which gives rise to the wave function Ψ_2. If, however, the stabilities of the different structures are more nearly equal, the lowering of the energy produced by resonance is relatively greater. It must be emphasized that in this phenomenon it is not a question of molecules of two or more structures existing in equilibrium with one another. The resonance vibration is so rapid that for many purposes we have to consider the electron as in a new state characteristic of the resonance process, and the resonance structure may have properties which are different from those of the states between which resonance occurs.

Resonance of this kind can occur only if the alternative structures contain the same number of unpaired electrons. Now in our description

of the hydrogen molecule, we have seen that resonance occurs on account of the alternative structures which can be produced by interchange of the two electrons from one atom to another. The two configurations have exactly the same energy, and so give rise to strong resonance bonding, and in each configuration the spins of the two electrons are paired. Apart from these two structures, however, there is the possibility of ionized molecules

$$H_A^+H_B^- \text{ or } H_A^-H_B^+,$$

in which the one atom gives its electron to the other and so permits the latter to build up a complete group of two (1*s*) electrons. In these ionized molecules the spins of the two electrons are again paired, and consequently resonance can occur between these structures and the structure of the normal co-valent molecule in which the atoms are held together by shared electrons. In this way a further lowering of energy can occur and calculation shows that in the actual H_2 molecule, about 5 per cent. of the bond energy results from resonance with the ionic form. That is to say, we must regard the actual H_2 molecule as involving not only the co-valent molecule

$$H - H$$

in which the atoms are held together by the exchange forces of the two electrons with opposite spins, but as involving also the ionized molecule

$$H^+H^-$$

in which one atom has given up its electron to the other. In the case of the H_2 molecule the co-valent form is very much the more stable of the two, and so the actual molecule has the properties of the co-valent rather than the ionic form, and since the two forms have very different stabilities, the resonance has comparatively little effect on either the bond energy or the interatomic distance. On the other hand, in the case of the molecule of hydrofluoric acid, HF, the ionized molecule

$$H^+F^-$$

and the co-valent molecule

$$H - F$$

have energies which are much more nearly equal, and hence the conditions are favourable for resonance between the ionized and co-valent forms, and the lowering of energy and decrease in interatomic distance are correspondingly great.

Resonance of this kind can occur not only in simple diatomic molecules, but between different possible forms of complicated molecules. In the case of benzene, C_6H_6, for example, it has long been known that

the six carbon atoms form a closed ring, but the distribution of the four valencies of each carbon atom in this structure was for a long time a matter of dispute. Fig. 58 shows some of the structures which were proposed, and each of these seemed to explain some of the properties of the substance, but none would account for all the facts. From the point of view of the wave mechanics, the actual structure of benzene is the result of resonance between these different structures. It can be shown that the pairing of electrons represented by the Armstrong-Baeyer structure (Fig. 58(*c*)) is equivalent to a combination of the pairings of the five structures represented by Figs. 58(*a*) and (*b*). The actual structure of benzene is thus the result of resonance between the three Dewar and the two Kekulé structures, and of those the Kekulé structures play the most important part. The resonance effect greatly stabilizes the molecule, so that the actual substance benzene has properties which are more than the sum of those to be expected from the mere addition of the properties of the different structures. It must again be emphasized that it is not a question of molecules of the different structures existing in equilibrium with one another. In a sense we may say that the structures *a*, *b*, *c* . . . represent the end points of the resonance vibrations, so that the molecule spends a short fraction of its time in these structures, but most of its time is spent in a form which is neither one structure nor the other, but is characteristic of the resonance process. It must also be appreciated that the frequency of the resonance process is so high (of the order of 10^{16} per sec.) that the resonance vibrations affect the electrons only, and the relatively heavy atoms are not to be regarded as oscillating with this high frequency. The atoms in molecules, and in crystals, do undergo vibration for other reasons, but the frequencies concerned are very much lower (*ca.* 10^{12}).

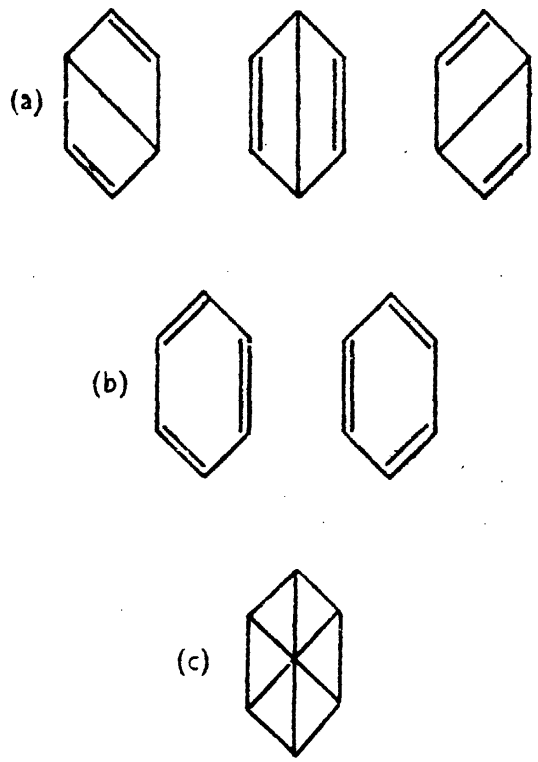


FIG. 58.—Older Structural Models for Benzene (C_6H_6).
(*a*) Dewar, (*b*) Kekulé, and (*c*) Armstrong-Baeyer.

In the molecule of benzene, there are 30 valency electrons, 24 of

which come from the carbon atoms and six from the hydrogen atoms. The resulting structure may be described by saying that 12 electrons are concerned in binding the six hydrogen atoms by co-valent bonds to the carbon atoms of the ring, whilst of the remaining 18 electrons 12 may be regarded as giving rise to single bonds within the ring, and 6 are associated with the benzene ring as a whole, and move freely in this ring in a configuration resulting from the resonance between the different structures of Fig. 58.

In the above description the term "resonance" has been used in connection with both the exchange effect in the co-valent bond (*e.g.*, the H_2 molecule, p. 131), and for the resonance which occurs between different structures such as those of the benzene molecule (p. 144). This is the accepted practice, and is the result of the two processes being mathematically similar, but it would undoubtedly be better if the term resonance were used for the second type of process alone. In the formation of the co-valent bond, the indistinguishability of electrons means that we cannot even in principle distinguish between the configuration with electrons No. 1 and 2 near to atoms *A* and *B* respectively, and that with electron No. 1 near to atom *B* and No. 2 near to atom *A*. Although the process is one of resonance, it would be clearer if it were called the exchange effect. The term resonance could then be used for the second type of phenomenon, in which resonance occurs between different structures such as those of the benzene molecule. It will be appreciated that in this case the different structures contain co-valent bonds in which the exchange effect has already taken place. Further, although the actual substance benzene always possesses the resonance structure, the different modifications (Dewar, Kekulé) could in principle be distinguished if one imagined them isolated.

The molecules whose structures have so far been described have been mainly those in which the atoms contain one, two, three, or four electrons fewer than the configuration of the next inert gas. In such cases, in the words of the simple Lewis theory, there are sufficient electrons present for it to be possible to build up stable octets (or a stable pair in the case of hydrogen) by means of normal electron sharing in which single, double, and triple bonds mean that two, four, or six electrons respectively are held in common between two atoms. In terms of the wave-mechanical theories, these elements contain sufficient electrons to fill completely all the bonding orbitals derived from the states of the valency electrons in the normal atoms. In the crystals of the elements which obey the $(8-N)$ rule, the normal valencies are satisfied by each atom sharing one electron with each of its $(8-N)$ neighbours. It is

clear that this process can proceed as far back as Group IV, but no further. In the diamond structure, each atom contains four valency electrons, and uses all of these to exert its maximum co-valency of four, and so acquires an octet. In the elements of Group III there are only 3 valency electrons per atom, and consequently only 3 co-valent bonds can be formed, whereas the atom must acquire 5 additional electrons if it is to build up an octet. It is thus impossible to build up an octet of electrons by means of co-valent bonds, and the same difficulty applies to an even more marked extent in the case of the elements of Groups I and II, where there are only one and two electrons per atom respectively. It can readily be shown that unstable structures would result if these elements formed ionic structures. For example, a structure in which $Cu^{-------}$ ions were surrounded by seven Cu^{+} ions which had given up their valency electrons to the central ion, would be most unstable, because the positive charge on the copper nucleus is not great enough to enable it to hold an octet of 4 quantum electrons firmly outside a $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10}$ core. We can thus readily see that on passing backwards from Group IVB, some new kind of atomic binding process will have come into being, because there are not sufficient electrons present to enable the atoms to build up octets by means of co-valent bonds. Reference to the Periodic Table will show that it is at this stage that the metallic elements * are found, and we can thus understand these as being the result of the constituent atoms containing too few electrons to build up stable groups by means of simple co-valent bonds. From the diagram of Fig. 54 it might at first be thought that the main characteristics of the elements of Group I would be the formation of diatomic molecules, since the lines for the $(\sigma_g\, ns)$ state slope downward from right to left and thus indicate bonding orbitals. Actually, molecules of formulæ Li_2, Na_2, and K_2 have been observed,† but these are not very stable, and all trace of them is lost in the metallic crystal, where each atom is surrounded perfectly symmetrically by the eight neighbours characteristic of the body-centred cubic structure.

In general, the metallic elements are characterized by the formation of monatomic vapours and of crystal structures of high co-ordination number, *i.e.*, structures in which each atom is surrounded by a large number of equidistant or almost equidistant neighbours. Under these conditions there are insufficient electrons to hold the atoms together by means of electron-pair or single electron bonds, and it has long been

* Boron in the First Period is probably non-metallic, but its crystal structure has not yet been determined, and its properties in a state of high purity are not yet known.

† Molecules of formulæ Cu_2, Ag_2, or Au_2 have not yet been observed.

recognized that in metallic cohesion, the valency electrons * are shared between the atoms, so that a metallic crystal may be regarded as consisting of an array of positive ions held together by attractions to the common system of negatively charged electrons. It has been suggested by Pauling that this metallic bonding may be regarded as an extension of the resonance process referred to above. In the case of the alkali metals, for example, the unit cell of the body-centred cubic structure has been shown in Fig. 38. This unit contains two atoms,† and consequently two valency electrons are available to bind the central atom to its eight neighbours. Pauling's suggestion is that the resulting condition of affairs is analogous to a resonance between all the different structures which might be obtained by allotting the electrons to definite one-electron or two-electron bonds between the various atoms. From some points of view this is merely another way of expressing the old idea that the valency electrons are shared between the atoms, but Pauling's method of approach to the problem serves to emphasize two important features. In the first place the interatomic distances in metallic crystals are usually of the same order as those to be expected for resonating, co-valent, or one-electron bonds. In the development of the theory of co-valency a large amount of data has been accumulated regarding the interatomic distances in crystals involving co-valent and resonance bonds, and in this way it has been found possible to deduce a set of atomic radii which account for the interatomic distances in this class of compound. These radii are approximately the same as those required to account for the interatomic distance in metallic crystals,‡ and this clearly suggests that the bonding process is essentially of the same nature.

In the second place, Pauling's views have served to explain why the metallic state of the elements extends to higher Groups of the Periodic Table in the elements of the A Sub-Groups than in those of the B Sub-Groups; for this purpose we consider the first two Short Periods as analogous to the B Sub-Groups. In the elements of the B Sub-Groups the orbitals available for bond formation are limited to four per atom, namely the one *s* orbital and the three *p* orbitals of the valency electrons. We can therefore understand why metallic structures cease at carbon,

* In the transition elements the cohesion involves not only the *ns* valency electrons, but also the outermost $(n-1)d$ electrons of the ion.

† The atoms at the eight corners of the unit cell are shared between eight units, and so may be regarded as each contributing $\frac{1}{8}$th of an atom to the cell under consideration. The atom at the centre of the cell belongs to this cell alone, and so counts as one atom. The total number of atoms associated with the cell is therefore two.

‡ There are slight corrections for variation in the co-ordination numbers in different structures, but these do not affect the general conclusion.

silicon, and germanium in the first three Periods, and at antimony and bismuth in the fourth and fifth Periods.* For when we have four electrons or more we have the possibility of filling the orbitals and building up stable groups of electrons. In the transition elements of the A Sub-Groups, we have already seen (p. 60) that the tendency is for the $(n-1)d$ electrons of the ions to have lower energies than the np states of the valency electrons. For these elements, therefore, there are five d orbitals of the ion available for bond formation as well as the s and p orbitals of the valency electrons. With four electrons per atom there is no possibility of filling all these orbitals, and consequently the metallic state continues past Group IV in the transition elements. This aspect of Pauling's theory is dealt with in detail in Part VI (p. 266).

In many of the earlier treatments of the subject, the reader will find it stated that the electrical conductivity of metals indicates that the electrons are free to move in metallic crystals, but not in crystals of other substances. This is, however, only partly true, and is sometimes a very misleading statement. In crystals of salts (including normal oxides),† the units of structure are the positive and negative ions, and there is little or no interchange of electrons from one ion to another. On the other hand, in co-valent crystals such as the diamond, the exchange effects (p. 131) mean that the electrons are continually moving from one atom to another, and the whole swarm of electrons is to be regarded as in continual circulation through the crystal. The difference between an insulator, such as the diamond, and a conductor is not that the electrons are bound in the one case and free to move in the other, but rather that in the conductor an external field can produce a resultant flow in a given direction. This, as we have already explained, means that the conductor must have unoccupied electron states into which the electrons may pass when the external field is applied. We can therefore begin to understand why the elements with comparatively few valency electrons per atom are those which show metallic conductivity. For if there are only a few electrons per atom, the available orbitals of the assembly (which are derived from those of the free atoms) will not be completely filled, and there will be unoccupied states in those orbitals into which the electrons can pass under the influence of an electric field.

After what has been said of the difficulties in solving a simple problem such as that of the H_2 molecule, it will readily be appreciated that the problem of the motion of electrons in a metallic crystal is

* We have already explained (p. 104) why lead does not crystallize in the diamond type of structure.

† There are some oxides which show what is called defect conductivity. In this process if an electron is missing from one O^{--} ion, an electron may jump from the next O^{--} ion. Here exchange forces may be present.

far too complicated to be solved in any detail. In the following chapters we shall describe some of the attempts which have been made to deal with the problem, and in these certain clear stages can be recognized. The first and most simplified treatment is to consider the behaviour of an assembly of electrons contained in an enclosed space, which is assumed to contain an atmosphere of uniformly distributed positive electricity so that the whole is electrically neutral. This free-electron theory or "electron box" model is described in Chapters XX to XXIII and is, of course, far too simplified to bear much resemblance to the state of affairs in most actual metals, but the theory is of great interest because it shows very clearly how an assembly of electrons at the concentrations concerned in solid metals has properties which are very different from those of an assembly obeying the classical gas laws. For some purposes the theory is a satisfactory approximation to the state of affairs in the alkali metals, but for other metals the main value of the free-electron theory is to provide a simplified background against which the characteristics of the more complicated theories can be seen most clearly. The next stage in the theory consists in examining the behaviour of an assembly of electrons moving in the periodic fields of the various crystal structures. This theory is due to Bloch, and is described in Chapter XXIII. In this treatment the electrons are regarded as moving in a simple periodic field which has the periodicity of the lattice, and the quantitative details of the field are not considered. This theory of electrons in a periodic field has been brilliantly successful, and has shown that when the periodicity of the field is of the order of 10^{-7} to 10^{-8} cm. (*i.e.*, the size of the unit cell of the crystal) the behaviour of electrons according to wave mechanics may be entirely different from that predicted by classical mechanics. In particular, it is possible to show that in a periodic field there are both permitted and forbidden energy states for the electrons, and in this way an explanation is obtained of the existence of the three main classes of substance—metals, semi-conductors, and insulators. In the final stage of the theory, attempts are made to work out the theory of the simple periodic field with greater quantitative detail. This leads to the introduction of electrons in *s* states, *p* states, &c., in the crystal, and is the mathematical development of the ideas shown in simple form in Figs. 27 and 52. Broadly speaking, it may be said that this part of the theory, which is described in Chapter XXVII of Part VI, has so far been rather disappointing. It has shown that some of the conclusions of the theory of the simple periodic field require modification when the problem is attacked in greater detail, but it has led to few if any really new ideas, and in many cases the problems have become involved in an immense

mass of mathematics from which a solution can only be obtained by the introduction of so many approximations that the final result is really of little quantitative value. The non-mathematical reader * must be warned that if he attempts to draw conclusions from papers of this class, it is nearly always necessary to seek advice from a professional mathematical physicist in order to appreciate the real significance of the calculated results. It is unfortunate that in many cases the results of numerical calculations are given to 3 or 4 figures even where the second figure is uncertain, and there is a singular reluctance on the part of some mathematical physicists to publish estimates of the uncertainty in the results which they claim to calculate.

* Thanks are due to Professor Mott and Dr. Fröhlich for having guided the present author past many snares of this type.

Suggestions for Further Reading.

Barrett, C. S. "The Structure of Metals. Crystallographic Principles, Techniques, and Data." New York: **1943** (McGraw-Hill Book Co., Inc.).

Born, M. "Atomic Physics." Translated by J. Dougall. London: **1946** (Blackie).

Hume-Rothery, W. "The Structure of Metals." London: **1945** (Institute of Metals).

Seitz, F. "The Physics of Metals." New York: **1943** (McGraw-Hill Book Co., Inc.).

PART IV.—THE FREE-ELECTRON THEORY OF METALS.

CHAPTER XX.—THE FERMI-DIRAC STATISTICS AND THE ELECTRON GAS.

IN Part III we have seen that when atoms are brought into close contact, the general effect is for each sharp energy level of the free atom to be broadened into a band which becomes wider as the atoms approach each other more closely. The exact details of the process in a crystalline solid constitute a problem of great complexity, and only approximate solutions are now available. Of these theories, the most simple is the so-called free-electron theory, in which the structure of the solid is ignored, and the metal is regarded as containing a number of electrons which move about freely as though they constituted particles of an electron gas. The electrostatic repulsion between the electrons is also ignored, and the model really involves the assumption that the



FIG. 59.

metal contains a uniformly distributed positive charge which neutralizes the charge on the electrons and enables the latter to be treated as ordinary gas particles of very small mass. It need scarcely be said that such an assumption is a great over-simplification of the problem, and, as we shall see later, the free-electron theory is a fair approximation to the state of affairs existing in the alkali metals, but is a very poor approximation for nearly all other metals. The theory is retained largely because it is a convenient approximation which lends itself to comparatively easy mathematical treatment, and also because it provides a simplified background against which the complexities of the more complete theories can be seen most clearly.

The free-electron theory assumes that the potential within the metal is constant, and that there is a sharp rise in the potential at the surface of the metal, which prevents the electrons from escaping. In problems of electronic emission, the exact form of the potential curve at the surface is of great importance, but for many other problems these details are unimportant, and it is customary to draw a potential diagram of the type shown in Fig. 59, where W represents the potential step at

the boundary. Comparison with experimental data suggests that W is of the order 10 e.v. for most metals. For many purposes it is customary to assume the zero of potential energy to be that of an electron at rest outside the metal, and in this case the energy of an electron within the metal is :

$$-W + \tfrac{1}{2}mu^2 \quad . \quad . \quad . \quad . \quad . \quad \text{IV (1)}$$

since the kinetic energy of a free electron is $\frac{1}{2}mu^2$, where u is the velocity. In comparing the conclusions of the theory with the experimental results for actual metals, the question of the variation of W has always to be considered. In more elementary developments, it is customary to assume that for a given metal W is independent of both temperature and volume. As regards the dependence of W on volume, this is quite unjustified, and some of the discrepancies between the conclusions of the theory and the experimental data for electronic emission are to be ascribed to the fact that the simple theory ignores the change in W resulting from the thermal expansion. It is less certain whether W is affected by temperature alone, apart from the effect due to thermal expansion.

For many purposes it is unnecessary to consider W, and it is often customary to take the zero of potential energy to be that of an electron at rest within the metal, in which case the energy of an electron is purely kinetic. This is the procedure adopted in the well-known text-book of Mott and Jones, but if this convention is used it must always be remembered that there is really a potential energy term which may be variable under some conditions. In their discussion of the subject, Fowler and Guggenheim * conclude that a calculation of the variation of W with temperature and volume is prohibitively difficult, and this prevents the free-electron theory from being used to explain phenomena connected with changes of pressure or volume.

One of the most useful features of the free-electron theory is that it shows in a simplified way some of the main differences between a "gas" of electrons at the densities at which electrons exist in solid metals, and an ordinary gas obeying the laws of the Classical Theory. We have first to consider how the state of a gas is to be described, and here if we adopt the older viewpoint, we may imagine the state of a gas molecule to be defined by its position (x, y, z) relative to three mutually perpendicular axes, and by the three components of momenta (p_x, p_y, p_z) parallel to the same three axes. If then we have a gas containing N molecules, the state of the whole gas at any instant can be represented by a single point in a so-called *Phase Space* of $6N$ dimensions, these

* R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics, Sections 1107 and 1118." London : 1939 (Macmillan & Co., Ltd.).

dimensions being (x, y, z, p_x, p_y, p_z) for each molecule. We could also describe the condition of a gas by an assembly of points in a *six-dimensional Phase Space*, where the dimensions are the three co-ordinates of position x, y, z and the three co-ordinates of momenta (p_x, p_y, p_z), and each point refers to one molecule of the gas. This six-dimensional phase space is called a *Molecular Phase Space*. We could also describe the momentum characteristics of a gas by an assembly of points in a so-called *Momentum Diagram* in which the three co-ordinates are the components of momenta (p_x, p_y, p_z) parallel to the three mutually perpendicular directions (x, y, z) in real space. In this case in the older statistics each particle is represented by a point P, such that the length OP (Fig. 60(a)) is equal to the momentum, and the direction OP gives the direction of motion of the particle concerned. The momenta of all the particles of a gas would then be represented by a dust or cloud of

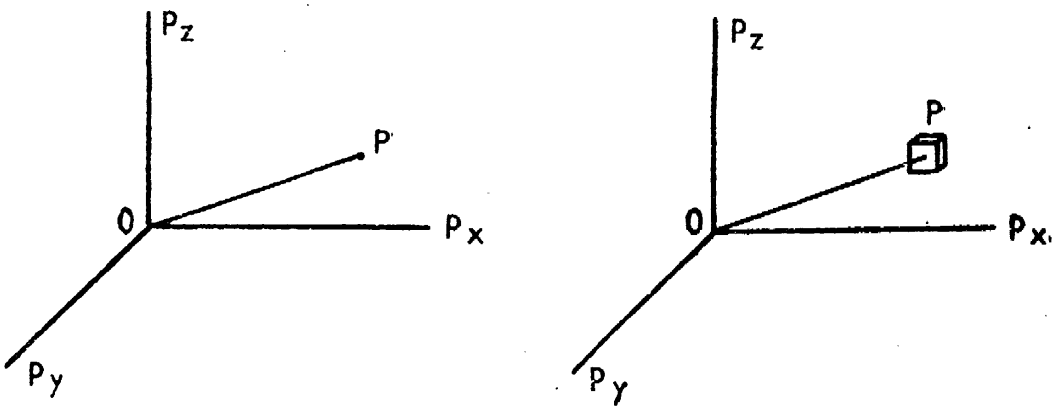


FIG. 60.

points in the momentum diagram, and the density distribution of this dust could indicate the energy of the assembly, a point near to the origin corresponding to a particle of low momentum, and hence of low velocity and small kinetic energy.

It will be appreciated that the momentum diagram by its very nature tells us nothing about the position of a molecule, but refers solely to the momentum. In the older statistics, where the mean energy of a gas particle was proportional to the absolute temperature, diminishing temperature resulted in the dust of points becoming more closely concentrated about the origin (*i.e.*, the velocities became smaller), and at the absolute zero all the dust points were concentrated with infinite density at the origin of Fig. 60(a).

In the new quantum statistics a momentum diagram analogous to that of Fig. 60(a) is still used, but the restrictions imposed by the Principles of Heisenberg and Pauli have to be considered, and for this purpose we may imagine the gas to be contained in a cube of side L,

and volume L^3. Since each particle is now restricted to a volume V, its momentum can no longer be specified exactly. The effect of this is to divide up the momentum diagram into little cells of volume h^3/V, since, if the particle is confined to a cube of side L, the uncertainty in its momentum must be at least h/L in each dimension, and so its momentum cannot be defined more precisely than as being associated with a volume h^3/V in the momentum diagram; it can be shown that this volume is independent of the shape of the metal. These cells become smaller as the volume of the metal increases, and each cell represents a quantum state. For an electron gas, in accordance with Pauli's Principle, each state can be occupied by not more than two electrons, and the statistical theory based on this assumption is known as the Fermi–Dirac statistics.

The Heisenberg Principle refers to the *minimum* uncertainties, and consequently when we come to consider an individual electron in a volume V, we can no longer regard it as definitely associated with one cell in the momentum diagram. We have instead to say that its momentum is most probably that of a particular cell, but that there are certain probabilities of its momentum being that of an adjacent cell, these probabilities diminishing as the values of the momentum differ from the most probable value. In the free-electron theory, the electrons are regarded as undergoing continual collisions with the atoms (or more properly the thermal vibrations of the lattice), as a result of which an electron is in a given energy state for only a very short time. According to Heisenberg's Principle, we can know the energy exactly only if the time is completely indeterminate, and consequently for electrons in a metal each energy state must have a corresponding width or uncertainty, and for any solid appreciably larger than atomic dimensions the width of the energy states is greater than the distance between them. This fact, together with the uncertainty in the momentum and the smallness of the constant h, means that it is justifiable to treat the energy states as forming a continuum, although Pauli's Principle still applies and there cannot be more than two electrons in each volume h^3/V of the momentum diagram.

The above remarks are based on the fact that we know the electron is within the volume V, but if we attempt to localize its position inside the volume, then the uncertainty in its momentum becomes correspondingly greater. If, for example, we consider the electron as travelling about inside the solid, we have to consider it as a probability wave-packet (see p. 44), and the more we localize its position the wider is the range of cells in the momentum diagram in which the momentum of the electron may lie. We have already seen (p. 43) that the position of the electron in real space can only be represented by a probability

wave-packet, which extends over a larger range, the more precisely we define the momentum of the electron. Similarly, the position of the point representing the momentum of the electron in the momentum diagram can be defined exactly only if the position of the electron is completely indeterminate. As soon as we place restrictions on the position of the electron, *e.g.*, by saying that it is in the volume or part of the volume V, there is an uncertainty in its momentum, and the representative point in the momentum diagram has to be replaced by a probability wave-packet, the amplitude of which at any place is a measure of the probability of the electron having the momentum concerned. In all ordinary problems the electron cells of volume h^3/V in the momentum diagram which represent the possible electron states are so small that the region in which the probability momentum wave-packet has an appreciable amplitude extends over many cells, and the more we localize the position of the electron, the larger is the volume of momentum space in which the representative point may lie. In the free-electron theory this point is not often of importance, but in the more complex theories where the atomic structure is considered the situation may be very different. If, for example, we consider an electron as moving between a given pair of atoms, we are localizing its position to within a distance of the order of 10^{-8} cm., and under these conditions its momentum will be correspondingly uncertain, and its point in the momentum diagram may lie in any one of a large number of cells.

As explained above, Pauli's Principle states that each cell in the momentum diagram can contain not more than two points, corresponding with electrons of opposite spins. At high temperatures and low densities this restriction on the number of points in each cell of the momentum diagram has little effect, since the dust of points is widely scattered (*i.e.*, the momenta and energy are large). But at low temperatures the restriction is of great importance, because it implies that at the absolute zero the dust of points can no longer contract to the origin. Since each cell of volume h^3/V can contain only two dust points, representing two electrons in the same state but with opposite spins, an assembly of N electrons must occupy at least $N/2$ cells, and hence a volume of momentum space equal to at least $Nh^3/2V$. At the absolute zero of temperature, the cells closest to the origin are each occupied by two dust points, and the lowest energy will clearly be when the distribution is symmetrical, so that the occupied states constitute a sphere in the momentum diagram, the volume of this sphere being given by the equation :

$$\frac{4}{3}\pi p_{\max.}^3 = \frac{Nh^3}{2V} \quad . \quad . \quad . \quad . \quad . \quad \text{IV (2)}$$

where $p_{max.}$ represents the momentum of the highest occupied state. If we adopt the convention that the potential energy of an electron at rest inside the metal is zero, the total energy of each electron will be kinetic, and will be equal to $\frac{1}{2}mu^2$, which equals $\frac{p^2}{2m}$, where p is the total momentum. It follows, therefore, that at the absolute zero, where the occupied states form a sphere round the origin of the momentum diagram, the energies of the electrons extend over a range from the almost zero value * of the lowest state, to a maximum value, $E_{max.}$, given by :

$$E_{max.} = \frac{1}{2m} p^2_{max.} = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3} = \left(\frac{3}{\pi}\right)^{2/3}\left(\frac{N}{V}\right)^{2/3}\frac{\pi^2\hbar^2}{2m}. \quad \text{IV (3)}$$

where $\hbar$ is an abbreviation for $\frac{h}{2\pi}$

The free-electron theory does, therefore, satisfy the first requirement of a satisfactory theory in that, even at the absolute zero, the electronic energies are spread over a range of values, which increases as the volume becomes smaller. It will be appreciated that as the volume of the metal becomes larger, the volume of the cells in momentum space (h^3/V) becomes continually smaller, so that the difference in the energies of successive states becomes smaller, and the magnitude of h is such that for any piece of metal of reasonable size, the difference between successive states or energy levels is so small that they may be regarded as forming a continuum. $E_{max.}$, however, depends not on V, but on N/V, and consequently for any given metal, $E_{max.}$ is independent of the size of the specimen, since if we double the volume we also double the number of electrons present. If the numbers of electrons present are of the order one per atom, the calculated values of $E_{max.}$ for most metals are of the order of 1 to 10 e.v. Thus Mott and Jones † give the following values of $E_{max.}$ for the univalent metals on the assumption of one electron per atom, using the accepted value of Avogadro's number, and the experimentally determined densities and atomic weights.

Element.	Li.	Na.	K.	Rb.	Cs.	Cu.	Ag.	Au.
$E_{max.}$, e.v.	4·74	3·16	2·06	1·79	1·53	7·10	5·52	5·56

For the alkalies, the method is a rough approximation, and the steady decrease in $E_{max.}$ with increasing atomic number is a result of the steady increase in atomic volume.

It will be seen, therefore, that the picture of an electron gas at the

* As explained in Chapter I (p. 20), the Heisenberg Uncertainty Principle prevents us from thinking of an electron in a finite volume as being at rest.

† "The Theory of the Properties of Metals and Alloys," p. 54. Oxford: 1936.

absolute zero of temperature, given by the Fermi–Dirac statistics is very different from that of the older statistics, since even at the absolute zero there are electrons of high energy, and it can be shown that the total energy of an assembly of N electrons at the absolute zero is $3/5NE_{max.}$, so that the mean energy of one electron, which is called the *mean Fermi Energy*, is $3/5E_{max.}$. For convenience we may replace $E_{max.}$ by the symbol ε^*, and this quantity is of great importance, because many of the equations for the properties of the electron gas can be expressed comparatively simply in terms of ε^*. The fact that many of the equations involve the constant π can be readily understood if the concept of a sphere of occupied states in the momentum diagram is borne in mind. The high energy of the electron gas at the absolute zero is the direct result of the Pauli Exclusion Principle, which prevents more than two electrons from occupying the same state. Other ways of expressing this principle are that the density of states in momentum space cannot exceed $2V/h^3$, and that the density of states in 6-dimensional phase space cannot be greater than $2/h^3$.

If, at the absolute zero of temperature, we introduce electrons into a box of definite volume V, an argument similar to the above shows that the number of electronic states with energy less than a given value, E, is :

$$\frac{V}{6\pi^2}\left[\frac{2m}{\hbar^2}.E\right]^{3/2}.$$

Consequently, as the electrons are introduced into the box, their number varies as $E^{3/2}$, where E is the energy of the highest occupied state.

The free-electron model thus requires the energies of the electrons to be spread over a range, and the properties of the assembly will clearly depend on how the electrons are divided among the possible energy states. We have explained in Chapter XIII how the $N(E)$ curves indicate the distribution of the energy states over the different ranges of energy. In the free-electron model it is clear that $N(E)$ will increase continuously with E, since the greater the energy the larger is the sphere in momentum space which corresponds to the value of E concerned, and hence the greater the number of states in the range E and $E + dE$. The exact expression is given by differentiating the above expression with respect to E, so that :

$$N(E)dE = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}.dE \quad . \quad . \quad . \quad \text{IV (4)}$$

The relation between $N(E)$ and E is thus parabolic, as shown in Fig. 61, and at the absolute zero of temperature the assembly of N electrons occupies the $N/2$ lowest electron states extending up to $E = \varepsilon^*$

and represented by the shaded area in Fig. 62. From the definition of $N(E)$ it follows that at the absolute zero the number of occupied electronic states in unit volume of the metal is equal to the shaded area, and the number of electrons is twice this value, since each state contains two electrons.

The preceding remarks refer to the absolute zero of temperature, where the electrons occupy the $N/2$ lowest energy states, which form a sphere round the origin of the momentum diagram in Fig. 60(*b*). The surface of this sphere may be called the *Fermi Surface*, and the electrons in states on the Fermi Surface have energy ϵ^* at the absolute zero. We have next to consider the effect of rising temperature, and how this affects the distribution of points among the cells of the momentum diagram. Since increasing temperature produces increasing energy, we shall clearly expect a tendency for the occupied states to move outward from the origin of the momentum diagram as the temperature is

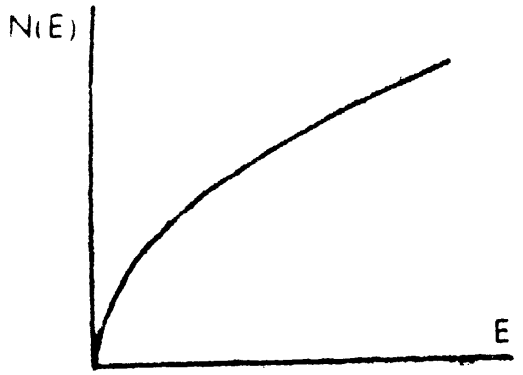


Fig. 61.

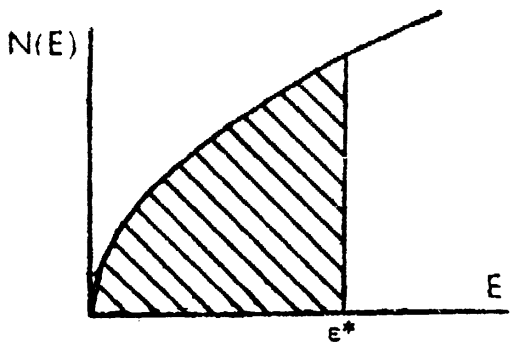


Fig. 62.

raised, and it is here that the Pauli Exclusion Principle produces one of its most striking effects. In the older statistics, a rise in temperature could produce an increase in the energy of any of the electrons, without any restrictions, but in the Fermi–Dirac statistics this is no longer so. Each cell in the momentum diagram of Fig. 60(*b*) can contain only two points, and consequently when the temperature is first raised above the absolute zero, an electron in a low energy state (*i.e.*, one near to the origin of Fig. 60(*b*)) cannot be raised to a state of slightly higher energy, because all these states already contain two electrons, which is the maximum allowed by Pauli's Principle. Electrons of low energy could therefore only undergo a large excitation, carrying them to the Fermi surface where unoccupied states exist, but the probability of such a large excitation is very small. Hence the first rise in temperature affects only those electrons in states near to the Fermi surface, since these can undergo excitation into adjacent states which are unoccupied. When, therefore, we first raise the temperature from the absolute

zero, the electrons of low energy are left unaffected, and only electrons with energies near ϵ^* are excited. As the temperature becomes higher and higher, continually greater numbers of electrons are excited, and at very high temperatures the excitation would affect the whole of the electrons, but at the electron densities concerned in metals these temperatures are far above the melting points. These general considerations apply also to the more complete electron theories, in which the first rise in temperature above the absolute zero again affects only the electrons near the Fermi surface. This statement does not, of course, imply that an individual electron in a low energy state always remains in that state. The statistical representation always allows interchange between electrons, so that electron No. 1 in state *A* and electron No. 2 in state *B* may interchange to give electron No. 2 in state *A* and No. 1 in state *B*. Since electrons are indistinguishable, it is doubtful whether this has any real meaning, and in any case the final and initial distributions are the same. The thermal excitation which we have been discussing involves the transition of an electron from one state to another with the production of a new distribution.

It remains to express these general considerations in a more precise form, and for this purpose we require a function showing the probability of finding an electron in a given state, or the probability that a given cell in the momentum diagram or the 6-dimensional phase space is occupied. This may be expressed by saying that the number of electrons in an element of 6-dimensional phase space $d\Phi$ is $2f d\Phi$, where f is the so-called distribution function, and the factor 2 arises from the fact that the electrons may have opposite spins. Since each volume h^3 of the 6-dimensional phase space corresponds with one state, this is equivalent to saying that the number dn of electrons per unit volume with velocities between the limits ξ, η, ζ, and $\xi + d\xi$, $\eta + d\eta$, and $\zeta + d\zeta$ is:

$$dn = 2\left(\frac{m}{h}\right)^3 f \,.\, d\xi \,.\, d\eta \,.\, d\zeta \quad . \quad . \quad . \quad . \quad \text{IV (5)}$$

and in the Fermi–Dirac statistics the function f is given by:

$$f = \frac{1}{e^{(E-\epsilon)/k\theta} + 1} \quad . \quad . \quad . \quad . \quad . \quad \text{IV (6)}$$

where $E = \frac{mu^2}{2} = \frac{m}{2}(\xi^2 + \eta^2 + \zeta^2)$ and ϵ is the thermodynamic potential of one molecule of gas; ϵ is thus given by: †

$$\epsilon = U - \theta S + pv \quad . \quad . \quad . \quad . \quad . \quad \text{IV (7)}$$

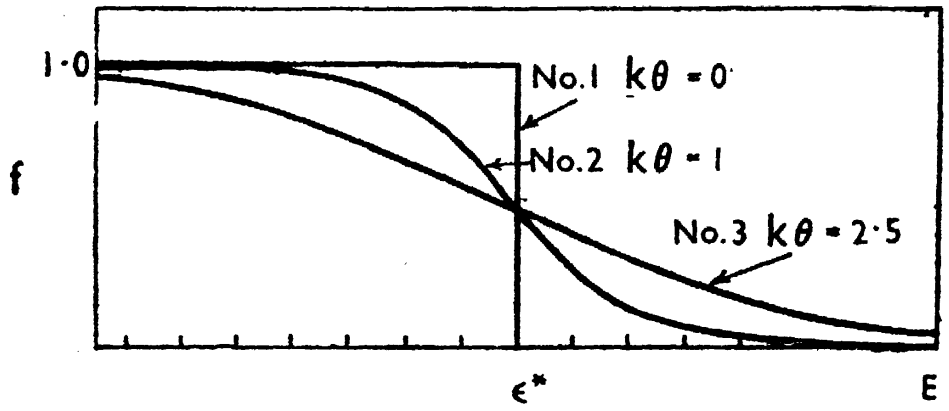
and is a function of temperature. At the absolute zero of temperature

† In this equation U is the total internal energy, θ the absolute temperature, S the entropy, p the pressure, and v the volume.

$z = \varepsilon^*$, so that at the absolute zero the thermodynamic potential is equal to the energy of the electrons on the Fermi surface. It can be shown that the variation of z with temperature is given by :

$$z = \varepsilon^* - \frac{\pi^2}{12}\frac{k^2\theta^2}{\varepsilon^*} \quad . \quad . \quad . \quad . \quad . \quad \text{IV (8)}$$

for the range in which the gas is almost completely degenerate. We have already seen that ε^* is of the order of 1 to 10 e.v., and since at 1000° C., $k\theta$ is only about $\frac{1}{10}$ e.v., it can be seen that z is approximately equal to ε^* at ordinary temperatures. At the absolute zero of temperature, since $E = \varepsilon^*$, it can readily be seen from equation (6) that if $E < \varepsilon^*$, $f = 1$, and that if $E > \varepsilon^*$, $f = 0$. If, therefore, we plot f against E, we obtain a curve of the type shown in Fig. 63, No. 1, with a sharp fall at $E = \varepsilon^*$. The meaning of this is that up to $E = \varepsilon^*$ all the states are occupied by two electrons, since $f = 1$, and $2f = 2$ in Fig. 63, whilst for



[*Courtesy McGraw-Hill Publishing Co., Ltd.*

FIG. 63.

energies greater than ε^* no state is occupied, the Fermi surface being perfectly sharp. At higher temperatures the corresponding curves take the form shown in Fig. 63, Nos. 2 and 3. These curves have the characteristic that they pass through the point $f = \frac{1}{2}$, $E = \varepsilon^*$, and are symmetrical with change of sign about this point. From the relative magnitudes of ε^* and $k\theta$, it will be appreciated that it is only at very high temperatures that there is any considerable difference from the curve at the absolute zero. The meaning of these curves is simply that as the temperature is first increased above the absolute zero, the electrons of low energy are left unchanged (*i.e.*, $f = 1$) and the states of low energy continue to be fully occupied, whilst some of those of higher energy are excited. This excitation means that there is a probability of finding electrons in states with $E > \varepsilon^*$, so that the value of f for these states is now greater than zero. This implies that the states for which E is slightly less than ε^* are no longer completely occupied, and so the value

of f for these states is less than unity. If we consider the electrons of highest energy for which $E - \epsilon^* \gg k\theta$, the number of electrons per energy range dE is, from the above equations:

$$2N(E)e^{-(E-\epsilon)/k\theta} \quad . \quad . \quad . \quad . \quad . \quad \text{IV (9)}$$

This is the equation for a distribution of a Maxwellian type, so that if $E = \epsilon$ is taken as the zero of energy, the electrons of highest energy have a Maxwellian distribution.

The curves shown in Fig. 63 indicate the probability of states of given energy being fully occupied at different temperatures.† We have next to consider the conditions which determine whether the state of a gas approximates to that at the absolute zero (curve No. 1 in Fig. 63). Gases in this state are said to be degraded or degenerate, and it can be shown that the condition for almost complete degradation ‡ is that:

$$\frac{Nh^3}{2V}(2\pi mk\theta)^{-3/2} \gg 1 \quad . \quad . \quad . \quad . \quad \text{IV (10)}$$

This condition is satisfied by all metals at ordinary temperatures, and even at 2000° K. the deviation is very slight. It will be noted that degradation is favoured by the small mass of the electron, and by large values of N/V, *i.e.*, by a high concentration of electrons in a given volume. Roughly speaking, a gas of electrons at ordinary temperatures at the densities concerned in metals is degraded to an extent which would correspond with that of a gas such as helium at a few degrees above the absolute zero, if it obeyed the Fermi–Dirac statistics. Actually helium obeys the Einstein–Bose statistics, and so the comparison cannot be made.§ For many purposes, therefore, electrons in metals at ordinary temperatures can be considered as completely degraded, and the equations for the behaviour at the absolute zero can be used, with a great simplification of the mathematical treatment. The first application of the Fermi–Dirac statistics to the problem of electrons in metals was made by Pauli ‖ in connection with the paramagnetic properties of the alkali metals (see p. 177). The whole subject was then developed by Sommerfeld ¶ in a remarkable series of papers which stimulated work in many countries. Although the simple theory of Sommerfeld is open to several objections, the application of

† Since there are two directions of spin, a state for which $f = 1$ contains $2f = 2$ electrons.

‡ The German word for the phenomenon is *Entartung*.

§ For information on the difference between the Fermi–Dirac and Einstein-Bose statistics, the reader may consult J. C. Slater's "Introduction to Chemical Physics." New York: **1939** (McGraw-Hill Book Co., Inc.).

‖ *Z. Physik*, 1926, **41**, 81.

¶ *Ibid.*, 1928, **47**, 1.

the Fermi–Dirac statistics in this way represents one of the great advances in the theory of metals. The earlier work was usually subject to the simplifying assumption that the electron gas was completely degraded. At higher temperatures, where the electron gas is partly degraded, the treatment becomes more complicated, and the equations have been discussed by Stoner.† At extremely high temperatures or very low densities where :

$$\frac{Nh^3}{2V}(2\pi mk\theta)^{-3/2} \ll 1 \quad . \quad . \quad . \quad . \quad \text{IV (11)}$$

the Fermi–Dirac statistics reduces to the ordinary classical Maxwell–Boltzmann statistics,‡ and the function f takes the form :

$$f = e^{(E-z)/k\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{IV (12)}$$

The mathematical treatment then again becomes simple, but this condition is never satisfied by electrons within a metal, although it is sometimes satisfied by an electron atmosphere outside a metal, and in some problems of electron emission we are really concerned with an equilibrium between a degenerate Fermi–Dirac gas of electrons inside a metal and a gas of electrons obeying the Classical Laws outside the metal.

The different curves of Fig. 63 are, of course, closely related to the energy of the electron gas, since they indicate the distribution of points in the cells of the momentum diagram. For the degraded gas of electrons, the energy may be expressed in the form :

$$E = N\left[\frac{3}{5}\varepsilon^* + \frac{\pi^2}{4}\frac{(k\theta)^2}{\varepsilon^*}\right] \quad . \quad . \quad . \quad . \quad \text{IV (13)}$$

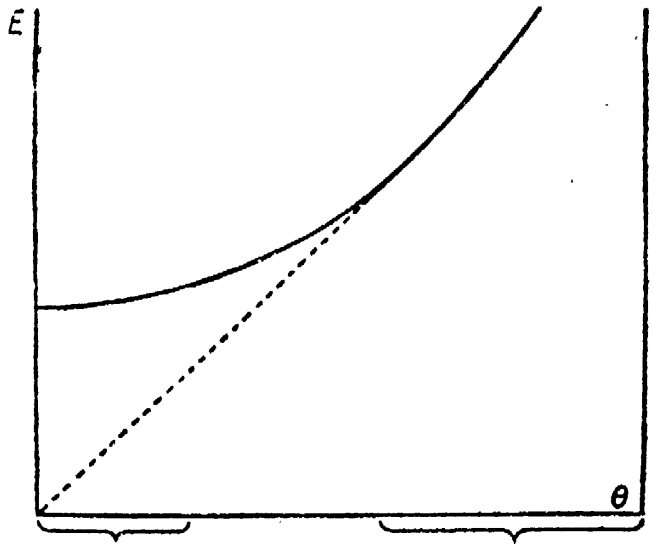
The relation between energy and temperature is of the form shown in Fig. 64, and a metal at ordinary temperatures corresponds with the almost horizontal part of the curve, so that the energy of the degraded electron gas is almost independent of the temperature. This is in marked contrast to the behaviour of an electron gas obeying the older

† *Phil. Mag.*, 1938, [vii], **25**, 899; 1939, [vii], **28**, 257.

‡ It may be noted that this condition is readily related to the Uncertainty Relation. Omitting the small numerical factors, equation IV (11) is equivalent to $\left(\frac{V}{N}\right)^{1/3}(mk\theta)^{1/2} \gg h$. Now $\left(\frac{V}{N}\right)^{1/3}$ is of the order of the average distance between two particles, and in classical mechanics $(mk\theta)^{1/2}$ is the average momentum. The product $\left(\frac{V}{N}\right)^{1/3}(mk\theta)^{1/2}$ is therefore of the same order as the product of the uncertainties in the momentum and position, and equation IV (11) states that this must be very much greater than h if classical mechanics is to apply.

statistics which required the energy to be directly proportional to the absolute temperature. Since the energy of a degraded electron gas is almost independent of the temperature, its specific heat is almost zero, and in this way we can understand why the specific heat of a metal can be explained by considering only the atomic vibrations, even though free electrons are present whose number is of the order one per atom. This is one of the great triumphs of the free-electron theory, and the general conclusion applies also to the more complete theories.

The specific heat of a degraded electron gas is obtained by differentiat-



[*Courtesy Clarendon Press.*

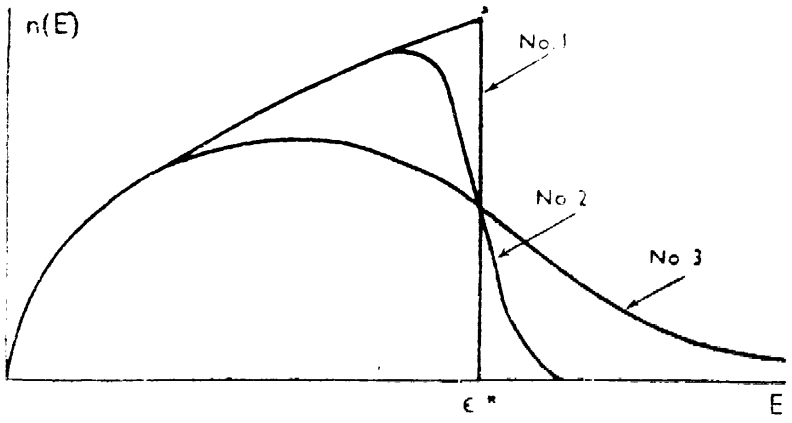
FIG. 64.

ing equation IV (13) with respect to the temperature, and, neglecting the small variation of ε^* with temperature, this is given by :

$$c_v = \frac{\pi^2 k^2}{2\varepsilon^*} N\theta \quad . \quad . \quad . \quad . \quad . \quad \text{IV (14)}$$

so that the electronic specific heat is proportional to the absolute temperature. At ordinary temperatures the specific heat of the electrons is negligible compared with that of the atoms, but at very low temperatures where the atomic heat has become small, the electronic specific heat is relatively much greater, and for some metals it has been possible to express the results of specific-heat measurements in the form of the sum of two terms, one representing the normal atomic heat, and the other being proportional to θ, and identified as being the electronic specific heat. These remarks refer to normal metals, but the transition elements often show abnormal specific heats for reasons which are described later (p. 266).

Fig. 63 shows the effect of temperature on the relations between f and E, and the corresponding effect on the $n(E)$ curve is shown in Fig.



[*Courtesy McGraw-Hill Publishing Co., Ltd.*

FIG. 65.

65, in which the vertical line showing the limit of the electronic energies at the absolute zero is replaced by curves of the form shown.

Chapter XXI.—The Models of Wave Mechanics.

In the above description we have referred to the Fermi–Dirac statistics, with the Pauli restriction of not more than two electrons in any one state, and we have accepted this as an arbitrary system which the electron gas obeys. It remains now to consider how this concept is related to the wave mechanics, and how the wave-like characteristics of an electron affect the electron gas. When we deal with the observed properties of metals such as electronic specific heat, electrical conductivity, thermal conductivity, electronic emission, &c., we are always concerned with the behaviour of a large number of electrons, and we are never able to follow the individual electron along its path. The requirements of a satisfactory theory are therefore that it accounts for the behaviour of large numbers or assemblies of electrons. The complete problem of the motion of electrons in an actual crystal where there is a periodic field disturbed by the thermal vibrations of the lattice is at present too difficult for solution, and even the problem of a gas of electrons which interact with one another (Coulomb repulsion, exchange forces, &c.) is very complicated; it is therefore necessary to begin by considering first the behaviour of one electron enclosed in a volume V, and to derive the wave-functions and the equations for the energy, &c. From this the theory goes on to consider the behaviour of an assembly of N electrons in a volume V, and it is assumed that the possible electron states are the same as those in the one-electron problem, subject only to the Pauli restriction that not more than two electrons are in any one state. So long as the assumption of non-interacting particles is accepted, this part of the theory is satisfactory, but it need scarcely be said that as regards the actual state of affairs inside a metal the treatment is a very great over-simplification of the problem, and to regard complete ψ patterns inside an actual metal as identical with those for one electron in an empty box of the same dimensions, raises as many difficulties as some of the inconsistencies of the older theories. Actually, as we shall see later, the free-electron model is usually a fair approximation to the condition of affairs in the alkali metals, but is a very bad model in nearly all other cases, and the theory is retained largely as a matter of mathematical convenience, and because it forms a simplified background against which the complexities of the more detailed theories can be viewed.

For convenience it is usual to assume that the metal exists in the

form of a cube of side L, and it is necessary to make some assumption as to the conditions which exist at the surface. Since the electrons exist within the volume $V = L^3$, the most simple boundary condition is clearly that ψ vanishes at the boundary, although in accordance with the general principles (p. 48) we shall not expect a sharp boundary. The wave function which satisfies this condition is of the form :

$$\psi = \sin\frac{\pi l_1 x}{L} \cdot \sin\frac{\pi l_2 y}{L} \cdot \sin\frac{\pi l_3 z}{L} \quad . \quad . \quad . \quad \text{IV (15)}$$

where l_1, l_2, l_3 are positive integers. If the zero of potential energy is that of an electron at rest outside the metal, and $-W$ is the potential inside the metal, the energies of the possible electron states are given by the relation :

$$E = -W + \frac{h^2}{8mL^2}(l_1^2 + l_2^2 + l_3^2) \quad . \quad . \quad \text{IV (16}a\text{)}$$

It is a general assumption of the theory that W is independent of the temperature, and the limitations of this have been discussed (p. 152). If we regard the potential inside the metal as zero, the expression for the energy, which is then purely kinetic, becomes :

$$E = \frac{h^2}{8mL^2}(l_1^2 + l_2^2 + l_3^2) \quad . \quad . \quad . \quad \text{IV (16}b\text{)}$$

which is the form used by Mott and Jones. The energies of the possible electronic states are thus characterized by the squares of three positive integers. Since $E = \frac{1}{2}mu^2$, and $\lambda = h/mu$, the wave-length of the lowest state is $2L/\sqrt{3}$ and corresponds with the combination $l_1^2 = l_2^2 = l_3^2 = 1$. The interval between successive energy levels is $h^2/8mL^2$, and since h is of the order of 10^{-27} erg-sec. and m is of the order of 10^{-28} g., the interval between successive levels becomes appreciable only when L is of atomic dimensions. As we have already explained (p. 154), when L is large compared with atomic dimensions, the energy levels are so close together that the Uncertainty Principle prevents us from saying that an electron is definitely in any one state, and the states may be regarded as forming a continuum, although the Pauli restriction still applies, and there cannot be more than two electrons to each state. An assembly of N electrons in a volume V, at the absolute zero of temperature, will thus occupy the $N/2$ lowest energy states given by equation IV (15), and this number $(N/2)$ will be equal to the number of sets of positive integers such that :

$$\frac{h^2}{8mL^2}(l_1^2 + l_2^2 + l_3^2) < E_{\max.} \quad . \quad . \quad . \quad \text{IV (17)}$$

where $E_{max.}$ is the energy of the highest occupied state. It can be shown that this is given by :

$$\frac{N}{2} = \frac{\pi}{6}\left[\frac{8mL^2}{h^2} \cdot E_{max.}\right]^{3/2} = \frac{V}{6\pi^2}\left[\frac{2m}{\hbar^2} \cdot E_{max.}\right]^{3/2} \quad . \quad \text{IV (18)}$$

This expression is the same as that on p. 157, so that the box model gives the Fermi–Dirac relation between E, V, and N. The ψ patterns given by the above equations may be regarded as those which fit conveniently into the cube of side L. They represent each electron state as a standing wave reflected from the sides of the box, but these standing waves are not to be interpreted as stationary electrons, but rather as indicating that there is an equal probability of finding the electron moving in one of two opposite directions. If the motion is referred to rectangular axes parallel to the three sides of the cube, then l_1, l_2, and l_3 are the direction cosines of the motion of the electron in the state defined by the integers l_1, l_2, and l_3.

For problems such as conductivity it is convenient to use a model in which the electron states are represented by travelling waves, and for this purpose what is called a " cyclical metal " is assumed. This may be regarded as an infinite metal divided up into small cubes of side L, and the boundary condition assumed is that ψ is triply periodic with period L, *i.e.*, that ψ repeats itself in each small cube so that the waves travel on continuously through the infinite crystal. The wave functions then assume the form :

$$\psi = e^{2\pi i(\chi_1 x + \chi_2 y + \chi_3 z)/L} \quad . \quad . \quad . \quad . \quad \text{IV (19)}$$

where χ_1, χ_2, χ_3 are whole numbers which may be either positive or negative, including zero. This model refers to an infinite metal with the internal periodicity given by the division into the small cubes of side L. To apply the argument to a metal of finite size, it is assumed that one single cube of side L can be treated with the same boundary condition, so that ψ is triply periodic with the period of the whole piece of metal of side L, but no condition is imposed to restrict the electron to the volume considered. Fortunately it can be shown that this does not affect many of the conclusions for the behaviour of the assembly of electrons as a whole, and the model is satisfactory as long as we are not concerned with properties near a surface.

The energies corresponding with equation IV (19) are :

$$E = -W + \frac{h^2}{2mL^2}(\chi_1^2 + \chi_2^2 + \chi_3^2) \quad . \quad . \quad \text{IV (20)}$$

where the χ integers are either positive or negative, including zero. If

W is assumed to be zero, the energy and wave-length of the lowest state are zero and infinite, respectively, as compared with the values $h^2/8mL^2$ and $2L/\sqrt{3}$ given by the box model. The fact that the integers in equation IV (17) are positive only, whilst those in equation IV (20) are positive and negative, results in the two models giving the same values for the number of energy states per unit energy range, and for all values of the properties of the swarm of electrons as a whole. The properties of the whole assembly of electrons are thus independent of the boundary conditions assumed, although the latter affect profoundly the energies, wave-lengths, &c., of the individual states. This point sometimes causes great confusion, since there is a natural tendency to ask whether the electron states in a metal are " really those " of equation IV (17), where the states are at intervals of $h^2/8mL^2$, or those of equation IV (20), where the intervals are four times as great. To answer this question we have to ask what we mean by reality, and if we adopt the attitude that this implies something measurable, then any method of measuring the energy will involve a certain error ΔE, and if the metal is large enough, *i.e.*, if L is large compared with atomic dimensions, the intervals between the successive energy states of the above equations will be smaller than ΔE. In this sense it may be said that the individual states of these equations have no real existence, although the energy of the assembly of electrons has a real existence and can be measured. The difference between successive energy states in equation IV (20) is four times as great as those in equation IV (17), but the existence of both positive and negative integers in equation IV (20) means that the density of states is four times as great as in equation IV (17), where the integers are positive only, and consequently both equations give the same results for the assembly as a whole, and both give the same result for the " reality " which we can measure; so that for a solid of ordinary size it is merely a matter of mathematical convenience which model is used. If, on the other hand, we were dealing with a very small solid, of dimensions of a few Ångstrom units, then the two equations would not be interchangeable, and on the whole we might expect the equations for the box model to be the more satisfactory, since this model contains the all-important condition that the electron is confined to the volume under consideration.

In the cyclic model, where the electron state is represented as a travelling wave, the individual electron must again be thought of as a wave-packet, and the mean velocity v associated with a state is given by the equation for the group velocity (p. 42) :

$$v = \frac{d\nu}{d\left(\frac{1}{\lambda}\right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{IV (21)}$$

Since the energy E is equal to $h\nu - mc^2$, this is equivalent to :

$$v = \frac{1}{h} \cdot \frac{dE}{d\left(\frac{1}{\lambda}\right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{IV (22)}$$

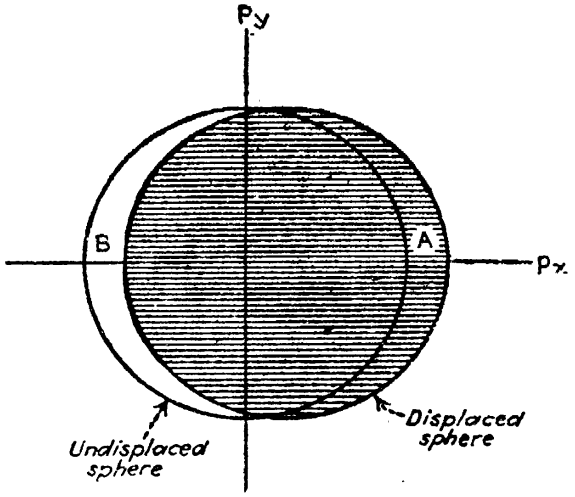
in problems where the velocity is small compared with c. For free electrons, the energy $E = h^2/2m\lambda^2$ and the mean velocity v associated with a state is given by $v = h/m\lambda$ and is equal to the root mean square velocity u. In the more complicated theories of Brillouin zones, equations IV (21) and (22) still apply, but the two velocities are in general not the same (p. 46).

Chapter XXII.—Applications of the Free-Electron Theory.

In Chapter XX we have seen how the specific heat of the degenerate electron gas is quite different from that of an ordinary gas obeying the classical statistics, and we have explained that these general ideas are carried over into the more complete electron theories. We may now consider briefly some other physical properties in which the general ideas of the free-electron theory apply to the more complete theories, even though the details require considerable modification.

(a) *Electrical Conductivity.*

For simplicity in drawing we shall consider a hypothetical two-dimensional metal, and in Fig. 66 we show a momentum diagram in



[*Courtesy McGraw-Hill Publishing Co., Ltd.*

Fig. 66.

which the two axes show the co-ordinates of momenta p_x and p_y. The full circle in Fig. 66 represents the Fermi surface; at the absolute zero of temperature, in the absence of an external field, this will be a sharp surface and perfectly symmetrical about the origin, and at a higher temperature the surface will be symmetrical but diffuse. If an electric field is now applied in the direction of the x-axis, the whole assembly of electrons will be accelerated in this direction, and the effect of this is to shift the Fermi surface bodily as shown by the shaded circle. This process would proceed indefinitely were it not for the "collisions with the atoms." The actual physical process is more properly described as an interaction between the electron and the thermal vibrations of the lattice. This is often called a "collision with an atom," because in the

earlier electron theories of metals the process was regarded as a collision between an electron, considered as a particle, and an atom; in some treatments it was even assumed that both the electrons and the atoms were spherical. It is now realized that any such precise picture is quite misleading, and that the real process involves the interaction between the thermal vibrations of the lattice and the wave system of the electron. It is, however, a convenient abbreviation * to speak of a " collision," and this is justifiable provided that the real nature of the process is borne in mind. The free-electron theory then makes the following assumptions regarding the collisions :

(1) That the collisions are nearly elastic, and that after each collision the electron sets out with a velocity whose direction is completely random. If the average time between two collisions is 2τ, it is customary to call τ the *time of relaxation*, and during the time 2τ, an electron has an acceleration in the direction of the field given by :

$$\frac{d^2x}{dt^2} = \frac{eF}{m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{IV (23)}$$

The average component of velocity in the direction of the field is thus zero immediately after a collision, and $2eF\tau/m$ after a time 2τ, when a further collision occurs, and the direction of motion is again quite random.

(2) That the changes in the velocities of the electrons produced by the field are small compared with their average velocities as particles of an electron gas.

The question then arises as to what restrictions are imposed on the collisions of the electrons on account of the degraded nature of the electron gas. Since the collisions are assumed to be nearly elastic, an electron can only be scattered into a state of nearly the same energy, *i.e.*, into a state at approximately the same distance from the origin of the momentum diagram of Fig. 60(*b*). In a degraded electron gas, all the states of low energy are fully occupied, and the conclusion is, therefore, that electrons of low energy cannot undergo collisions to cause a resistance. The electrons of low energy occupy the close-packed states round the origin of the momentum diagram, and this group of electrons produces no resultant flow in any direction, since for each two electrons with velocity $+ v$ there are two with velocity $- v$, and since the states are fully occupied no change in the distribution can be produced by collisions. Two electrons in low energy states

* This avoids the continual use of expressions such as " the interaction between the electron and the thermal vibrations of the lattice."

may, of course, interact with the lattice vibrations in such a way that if electron No. 1 is in state A before the collision, and electron No. 2 in state B, then after the collision electron No. 2 is in state A, and electron No. 1 is in state B. Since electrons are indistinguishable, it is a matter of definition whether this has any physical meaning, and in any case it does not cause a resistance, because the final state is the same as the first state. On the other hand, electrons at the edge of the Fermi surface, *i.e.*, those in the two crescents of Fig. 66 can undergo collisions, the general effect of which is to carry the point in the momentum diagram from the right-hand to the left-hand crescent, and so to create a resistance, and to set up a steady state in which the movement of the crescent to the right-hand of Fig. 66 is balanced by the throwing back of the representative points to the left. The condition of affairs is, therefore, one in which all the electrons are accelerated in the direction of the electric field, and all take part in the conductivity process, but only those at the edge of the Fermi surface can produce a resultant flow in any direction, or undergo collisions which produce a resistance.

The expression deduced by Sommerfeld for the electrical conductivity of a degraded electron gas is of the form :

$$\sigma = \frac{8\pi e^2 l}{3h}\left(\frac{3N}{8\pi V}\right)^{2/3} \quad . \quad . \quad . \quad . \quad \text{IV (24)}$$

Hence l is the mean free path of the electrons *at the edge of the Fermi zone*,* so that if $\bar{u}$ is the velocity of these electrons, l is defined by the relation :

$$l = 2\tau\bar{u} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{IV (25)}$$

The variation of conductivity with temperature has then to be ascribed to the variation of l, which cannot be calculated. The theory is unsatisfactory, because when numerical values are inserted the mean free path is of the order several hundred times the interatomic distances, and a free path of this magnitude is incompatible with the details of the calculation which involve the assumption of free gas particles colliding with spherical atoms. The long free paths can be understood, since wave mechanics permits an electron to move unimpeded through a perfectly regular lattice, but this involves the more detailed theories described later.

Just as a difference of electric potential causes a drift of electrons, so when a difference of temperature is set up between two parts of a

* It should be noted that the mean free path l of the Sommerfeld theory has not the same meaning as that of the older theories. In the Sommerfeld theory $l = 2\tau\bar{u}$, where $\bar{u}$ refers to the electrons at the edge of the Fermi surface; whereas in the older theories $l = 2\tau u$, where u is the root mean square velocity of all the electrons.

metal, the electron gas carries energy from the hot to the cold parts, and in this way the thermal conductivity is accounted for. The expression obtained by Sommerfeld is :

$$K = \frac{8\pi^3}{9} \cdot \frac{lk^2\theta}{h} \left(\frac{3N}{8\pi V}\right)^{2/3} \quad . \quad . \quad . \quad . \quad \text{IV (26)}$$

where θ is the temperature on the absolute scale. The fact that the thermal conductivity is almost independent of temperature at normal temperatures has again to be ascribed to the appropriate variation of l with θ.

The *Wiedemann–Franz Ratio*, *i.e.*, the ratio of thermal to electrical conductivity, is thus, according to Sommerfeld :

$$\frac{K}{\sigma} = \frac{\pi^2}{3}\left(\frac{k}{e}\right)^2\theta = 2{\cdot}45 \times 10^{-8}\left(\frac{\text{volts}}{\text{degree}}\right)^2 \quad . \quad . \quad \text{IV (27)}$$

This expression is independent of l, N, and V, and the theory thus predicts that K/σ has a constant value for all metals at a given temperature (the Wiedemann–Franz Law), and that the ratio varies in direct proportion to the absolute temperature (Wiedemann–Franz–Lorentz Law), and not merely are these predictions in general agreement with the facts, but the numerical value is very nearly correct. Actually the theory proves a little too much, since there are real differences between the values of K/σ for the different metals, even when allowance is made for the part of the thermal conductivity due to the atoms, as distinct from the electronic thermal conductivity.

The free-electron theory is by its very nature unable to deal with any of the problems involving the dependence of electrical conductivity on direction relative to the crystal axes. As a quantitative theory its value is not very great, because although the correct value of the Wiedemann–Franz ratio is obtained, this is only by the cancelling of the l terms, which are recognized as having magnitudes incompatible with the mathematical treatment. The general conclusion that the electrons at the edge of the Fermi surface are those effective in determining the resistance is, however, quite correct, and is developed in greater detail in the more complete theories.

(b) *Electronic Emission Phenomena.*

In dealing with emission properties it is usual to denote the potential energy of an electron at rest outside the metal as zero, and in the free-electron model, the potential inside the metal has a constant value $-W$, as shown in Fig. 67. At the absolute zero of temperature, the electrons occupy the $N/2$ lowest energy states extending up to the value ε^*. The minimum amount of energy required to expel an electron is therefore $(W - \varepsilon^*)$, in contrast to the picture presented by the classical

theory in which, at the absolute zero, the amount of work required to expel an electron was W, since the electrons were at rest. The experimental results then indicate that W is of the order of 10 e.v., and $(W - \varepsilon^*)$ is usually of the order 2–5 e.v.

We may consider first the process of photoelectric emission in which the electron absorbs a quantum of energy $h\nu$, where ν is the frequency of the radiation. It is clear from Fig. 67 that at the absolute zero emission will only take place if $h\nu$ is greater than $(W - \varepsilon^*)$, so that there will be a sharp threshold frequency given by :

$$h\nu = (W - \varepsilon^*) \quad . \quad . \quad . \quad . \quad . \quad \text{IV (28)}$$

Further, since ε^* is approximately constant at low temperatures, the threshold frequency should be almost independent of temperature, and this is in agreement with the facts. To a higher degree of accuracy, as the temperature is raised, the Fermi surface is no longer completely sharp, and the threshold frequency should no longer be completely sharp; this is in agreement with the experimental data, although up to

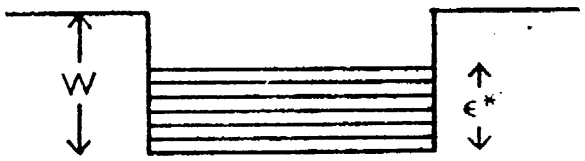


FIG. 67.

room temperatures the effect is very small. At higher temperatures the Fermi surface becomes more and more diffuse, and the process of photoelectric emission becomes increasingly complicated and becomes mixed with that of pure thermionic emission.

It is, of course, well known that electrons are emitted from metals at high temperatures, quite apart from any photoelectric effects. This process of thermionic emission has been studied from the viewpoint of the free-electron theory by two different methods. On the one hand, equilibrium between the electrons inside a metal and those in the surrounding space is treated from the viewpoint of the new statistics. On the assumption that the number of electrons emitted per second is equal to the number striking the surface per second, the theory leads to an equation of the form :

$$I = A\theta^2 e^{-B/\theta} \quad . \quad . \quad . \quad . \quad . \quad \text{IV (29)}$$

where I is the emission current, and A and B are constants, B being known as the thermionic work-function. This differs from the corresponding equation of the classical theory, which was of the form :

$$I = C\theta^{\frac{1}{2}} e^{-D/\theta} \quad . \quad . \quad . \quad . \quad . \quad \text{IV (30)}$$

and this difference is the result of the fact that the new statistics require the specific heat of the electrons within the metal to be zero. The two equations are in almost equally good agreement with the experimental data, although the equation involving θ^2 is the more correct.

In the second line of approach, the problem of penetration of the surface by electrons is considered from the standpoint of wave mechanics. It can be shown that only the energy associated with the component of velocity perpendicular to the surface need be considered, and the problem becomes one of the passage of wave trains (representing the electrons) through changes of potential occurring at the surface. When an electron moves away from the surface, it induces a charge on the metal and this gives rise to an image potential which attracts the electron back towards the metal. This image potential is equal to $-e^2/4x$, where x is the distance from the surface, and e is the electronic charge. The result of this is that the simple potential step of Fig. 68(a) becomes modified to that of Fig. 68(b). It can be shown that only the component of the velocity normal to the emitting surface need be

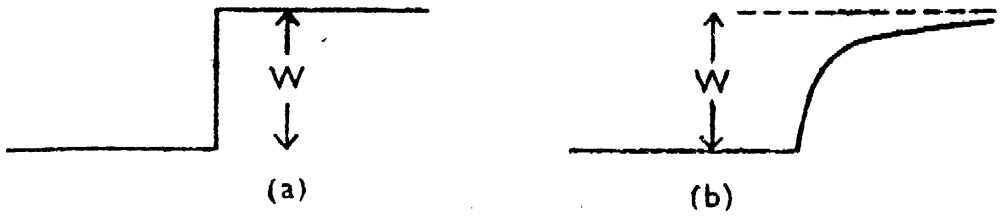


FIG. 68.

considered, and if E_n is the kinetic energy due to the velocity component normal to the surface, the emission current may be expressed in the form :

$$I = e\int_0^\infty N(E_n)D(E_n)dE_n \quad . \quad . \quad . \quad . \quad \text{IV (31)}$$

Here the potential inside the metal is taken to be zero, and $N(E_n)$ is the number of electrons with energy E_n which strike unit area of the surface in unit time, and $D(E_n)$ is the fraction transmitted. The Sommerfeld theory leads to the relation :

$$N(E_n)dE_n = \frac{4\pi m}{h^3} k\theta \log\left(1 + e^{-(E_n - Z)/k\theta}\right)dE_n \quad . \quad \text{IV (32)}$$

where Z is the thermodynamic potential of an electron. In the older theories, where the electron has only the properties of a charged particle, we shall expect the electron to remain within the metal if E_n is less than W, and to escape if E_n is greater than W. The wave-like properties of the electron produces a more complicated state of affairs in which the electron is still unable to escape if E_n is less than W, but in which the

value of D for the electrons which do escape depends on the exact form of the potential boundary. For the potential step of Fig. 68(a), the mean value of D for $E_n > W$ is about $\frac{1}{2}$, whilst for the more correct picture of Fig. 68(b) the mean value of D for $E_n > W$ is nearly unity.

On substituting equation IV (32) into IV (31) and integrating, we obtain for the model of Fig. 68(b), where $D = 1$:

$$I = \frac{4\pi mek^2}{h^3}\theta^2 e^{-(W-Z)/k\theta} \quad \text{IV (33)}$$
$$= 120\theta^2 e^{-(W-Z)/k\theta} \text{ amp./sq. cm.}$$

This is of the correct form if $(W - Z)$ is taken to be constant, except that the factor 120 is about double the correct value. This discrepancy may be ascribed to the fact that the treatment ignores the volume expansion of the metal which affects the potential energy. It is interesting to note that the over-simplified model of Fig. 68(a) gives almost the correct value for the thermionic constant, but this is fortuitous.

The above remarks refer to clean metals, but if a surface film is

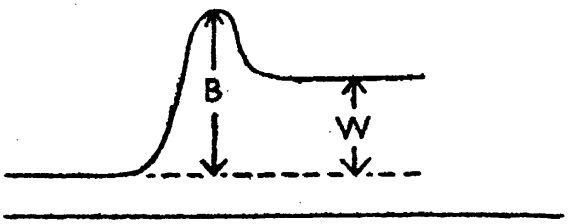


Fig. 69.

present, the wave-like properties of an electron produce very interesting results. If, for example, the potential step at the surface is of the form shown in Fig. 69 the older theories would allow an electron to escape only if its kinetic energy were greater than B, where B is the height of the potential hill due to the surface film. But according to wave mechanics, if the film is not too thick, the electron has a chance of escaping if its kinetic energy normal to the surface is greater than W, so that electrons can escape which could not do so according to the older theories. In this case the emission is still given by an equation of the type IV (29), but with reduced values of A and B.

(c) *Magnetic Properties.*

The simple free-electron theory does not deal with ferromagnetism or with the abnormal paramagnetism of transition elements such as platinum. For simple metals such as the alkalies, the free-electron theory indicates two effects, a paramagnetic effect due to the electron

spin, and a diamagnetic effect due to the translational motion. In comparing the theoretical conclusions with experimental results, allowance has to be made for the fact that the theory deals only with the effects of the free electrons, whereas the observed results include also the effect of the ions. All ions with complete outer electron groups of 8 or 18 electrons are diamagnetic, whilst some of the ions of transition elements are paramagnetic. In comparing theory and experiment great care is necessary to ensure that the observed magnetic properties are not affected by the presence of ferromagnetic impurities.

We may consider first the paramagnetism and imagine that we have an electron gas containing N electrons which at the absolute zero in the absence of a magnetic field occupy the $N/2$ lowest energy levels as shown in Fig. 70(a). We may now imagine that a magnetic field of strength H is applied, and we may consider the electrons with spins parallel and anti-parallel to the field, respectively. The energy of each

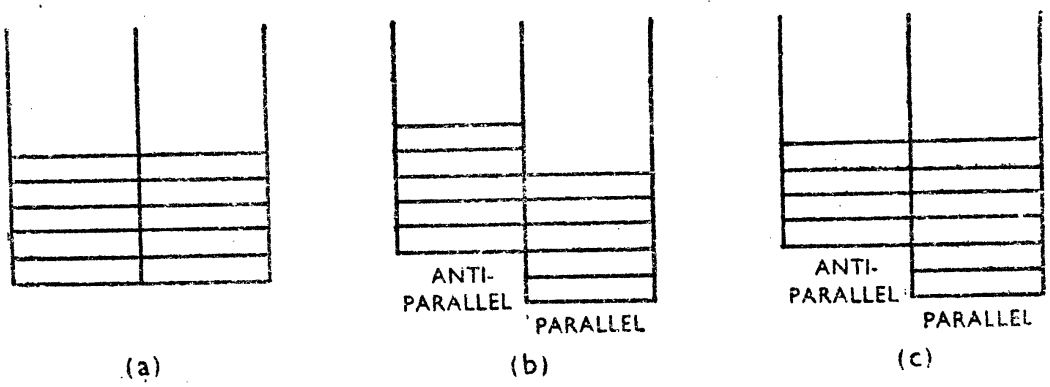


FIG. 70.

electron with parallel spin will then be diminished by an amount $H\mu$, where μ is the Bohr Magneton (p. 63) given by :

$$\mu = \frac{eh}{4\pi mc} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{IV (34)}$$

Similarly, the energy of the electrons with anti-parallel spins will be increased by $H\mu$, and the condition of affairs will be as illustrated in Fig. 70(b). It is clear that the energy of the system can now be diminished if some of the electrons with anti-parallel spins change to those of the parallel type. This change produces a decrease in magnetic energy of $2H\mu$ for each electron concerned, but since a given state can contain only one electron of a given spin, the electrons undergoing this reversal must enter states lying above those already occupied by the electrons with parallel spins, and there is thus an increase in kinetic energy. This process will continue until an equilibrium state is reached in which the increase in kinetic energy during a transfer is equal to the decrease in

magnetic energy so that the total energy (magnetic + kinetic) is unaffected during a transfer (Fig. 70(*c*)). There will thus be an excess of electrons with parallel spins, and hence a paramagnetic effect. The fact that the observed paramagnetism is almost independent of the temperature is merely the result of the electron gas being almost completely degraded at ordinary temperatures. To a first approximation the expression for the paramagnetic volume susceptibility is :

$$\kappa = \frac{3}{2} \cdot \frac{N\mu^2}{\varepsilon^*} \left[1 - \frac{\pi^2}{12} \left(\frac{k\theta}{\varepsilon^*} \right)^2 \right] \quad . \quad . \quad . \quad \text{IV (35)}$$

where the second term in the square bracket is extremely small. The numerical constants are such as to make κ of the order of 10^{-6}, which is in agreement with the experimental data. Equation IV (35) is in marked contrast to the conclusions of the classical theory, which required the susceptibility to vary inversely as the absolute temperature.

According to Classical Mechanics, the diamagnetic susceptibility resulting from the translatory motion of the particles of an electron gas is zero. In quantum mechanics this is no longer the case, because the electron moves in circular orbits round the direction of the field, and these orbits have to satisfy the quantum conditions. The theory works out in such a way that the diamagnetic susceptibility of the electron gas is numerically one-third of that given by the equation IV (35) for the paramagnetic susceptibility due to the spin. Consequently, the total paramagnetic susceptibility of an electron gas is two-thirds of that indicated by equation IV (35).

Suggestions for Further Reading.

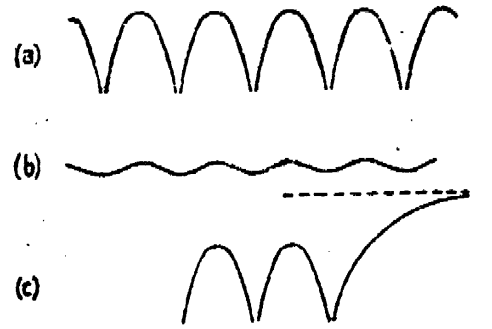
N. F. Mott and H. Jones, " The Theory of the Properties of Metals and Alloys." Oxford : 1936 (Clarendon Press).

A. Sommerfeld and H. Bethe, " Elektronentheorie der Metalle." (Handbuch der Physik. Zweite Auflage. Band XXIV. Zweiter Teil.) Berlin.

PART V.—THE BRILLOUIN-ZONE THEORY OF METALS.

CHAPTER XXIII.—THE SIMPLE THEORY OF BRILLOUIN ZONES.

THE simple free-electron theory imagines the electrons to move in a field of constant potential, and the next development of the theory consists in applying the wave mechanics to the motion of an electron in a periodic field. If we were to take a line passing through the centres of the atoms in a metal, the potential energy would vary with the distance as shown in Fig. 71(*a*), where there is a singularity at each atomic nucleus. The variation of potential along a line parallel to the first, but not passing through the centres of the atoms, would be as shown in Fig. 71(*b*), whilst Fig. 71(*c*) shows the variations of potential at the surface. The valleys in the potential curves are at distances of the order of 10^{-8} cm., and consequently, as explained before (p. 176), electrons of low energy have a probability of passing from one valley to the next even though their energies, according to classical mechanics, would not be sufficiently great to enable them to surmount the peaks. Electrons with energies greater than that of the peaks in Fig. 71(*a*) can, of course, move freely through the crystal in both classical and wave mechanics, but it is only in wave mechanics that the electrons of low energy are free to move.



[*Courtesy Clarendon Press.*
FIG. 71.

The theory of electrons in a potential field was first developed in its most general form by Bloch, and different simplified models were then examined by Brillouin, Peierls, Mott, Jones, and other investigators. We shall describe first the case where the variation in potential is small compared with the total kinetic energy of the electrons, and shall indicate which conclusions apply to the more general case.

In Chapter XX we have described the use of a momentum diagram. For a free electron, the wave-length, λ, is given by:

$$\lambda = \frac{h}{mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{V (1)}$$

where u is the velocity, so that the wave number, or the number of waves per unit length, is given by :

$$\frac{1}{\lambda} = \frac{mu}{h} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{V (2)}$$

Instead of a momentum diagram, we could therefore have used a wave-number diagram, since the wave number $1/\lambda$ is directly proportional to the momentum. For the purposes of the present theory, it is customary to multiply the wave number $1/\lambda$ by 2π, and the resulting quantity is termed the wave number k, defined by :

$$k = \frac{2\pi}{\lambda} = \text{(for free electrons)}\ \frac{2\pi mu}{h} \quad . \quad . \quad . \quad \text{V (3)}$$

We may thus construct a diagram in k-space exactly in the same way that we used a diagram in momentum space. If Fig. 72 represents three-dimensional k-space, the three axes k_x, k_y, k_z correspond to wave motion parallel to the x, y, and z axes of real space. In general, x, y, and z will be chosen so that they are related to the axes of the crystal, and in the cubic system, for example, k_x, k_y, and k_z will correspond with waves moving in the directions of the sides of the unit cell. The distance from the origin O of k-space to a point such as A represents the value of k for the electron state concerned, and the direction OA is the direction of the waves associated with the state A. In the free-electron theory, OA is also the direction of motion of the electron itself, considered as a wave packet or wave group built up from a number of states in the region of A. In the periodic field this is not necessarily so, and in general the group velocity of the waves of an electron in states near to A is not in the direction OA. That is to say, individual states in the region of the point A in k-space correspond with wave motion in the direction OA, but these waves combine together to form a wave group or wave packet which, in general, does not move in the direction OA.* Much of the difficulty in understanding the

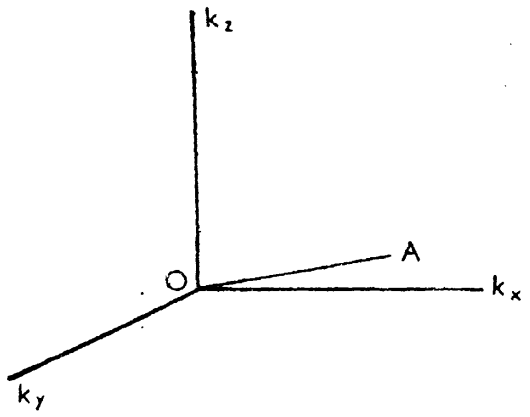


FIG. 72.

* In many descriptions the reader will find k or $\frac{h}{2\pi}k$ referred to as the momentum. The reason for this is that when a field of force is applied, the rate of change of $\frac{h}{2\pi}k$ is equal to the force, so that k satisfies Newton's definition of momentum. In the free-electron theory k is proportional to mass × velocity, but

theory lies in the result of a failure to realize this distinction between the direction of motion of the waves and of the wave group, and the reader must appreciate that in a periodic field it is quite possible for waves moving in one direction to build up a wave packet which moves in another direction.

In our description of the free-electron theory, we described the concept of a Fermi surface of occupied states. In the free-electron theory the Fermi surface is spherical, and we can imagine a number of concentric spheres in momentum space, or in k-space, the surfaces of which represent states of equal energy, and may therefore be called energy contours. The direction of motion of an electron in the free-electron theory is then perpendicular to the energy contour at the position of the point in k-space concerned.* In the same way, in the theory of the periodic field, we may again construct energy contours, or surfaces of constant energy in k-space. In general, these surfaces are not spherical (see p. 185), but the direction of motion of the electron (*i.e.*, the group velocity of the waves) is again perpendicular to the energy contour at the point concerned in k-space. Just as in a momentum diagram a point near to the origin represents a state of low momentum, so in k-space a point near the origin represents an electron in a state of low wave number. In the free-electron theory, the kinetic energy of an electron E and its wave number k are related by the simple equation :

$$E = \frac{h^2k^2}{8\pi^2m} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{V (4)}$$

which is independent of the direction of k; but the effect of a periodic field is to make the relation between E and k more complicated, and dependent upon the direction of k.

The theory is developed on the assumption of the cyclic model already described in connection with the free-electron theory, and is therefore able to deal with problems involving the flow of electrons in a definite direction. The theory assumes further that in considering the motion of any one electron the remaining electrons may be regarded as smoothed out throughout the crystal, so that the one electron under consideration moves in a strictly periodic field. Subject to these

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in the periodic field, as we shall see later, this is no longer so, and we may have a high value of k with a zero velocity. For this reason it seems to us better not to call k or $\frac{h}{2\pi} . k$, the momentum, because there is a natural tendency to visualize momentum as mass × velocity.

* The motion of the electron is, of course, in real space, but since the axes in k-space are chosen to correspond with directions of motion of waves in real space, it is customary to speak of motion parallel to a direction in k-space.

assumptions, the wave equation for the motion of an electron in a periodic field is of the form :

$$\psi = e^{i(kr)}\phi_k(x, y, z) \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{V (5)}$$

where ϕ is a function which depends in general on k, and has the three-fold periodicity of the lattice. This equation is general, and applies to all regular periodic variations in potential, and it may be compared with equation IV (19) of the free-electron theory. Equation V (5) represents a plane wave of wave-length $2\pi/k$ travelling in the direction of the vector k, but the wave is modulated in the rhythm of the lattice. Examination of this equation by the methods of wave mechanics then shows that there are only certain values of the energy for which k is real, and that for other values of the energy k would be imaginary.

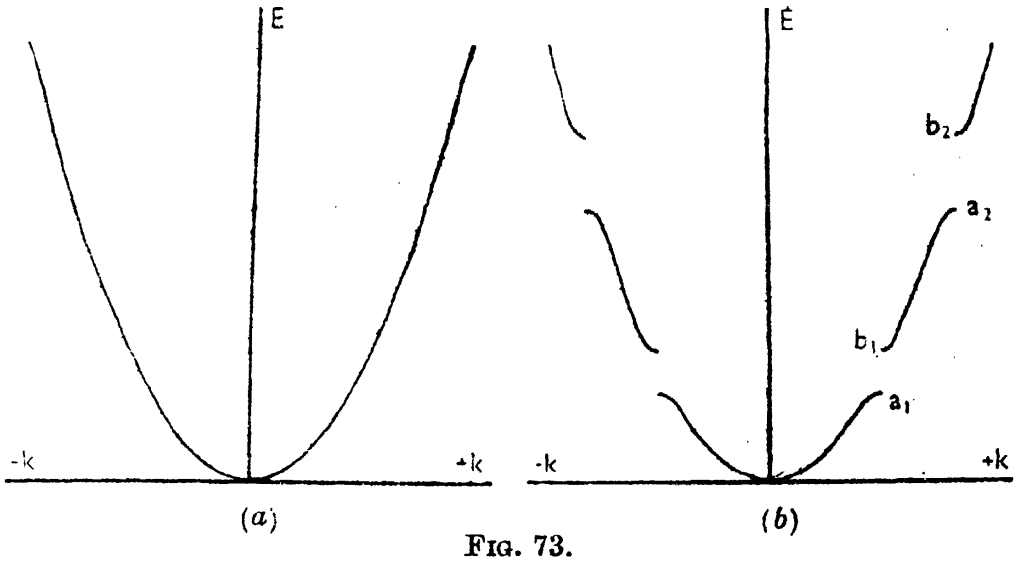


FIG. 73.

From this it is concluded that if we consider electron states corresponding with any one direction in k-space, the energies will not be a continuous function of the wave numbers, but will show gaps of forbidden energies.

The general conclusions of the theory are best understood by considering first a hypothetical one-dimensional metal, in which the potential undergoes a regular periodic variation as shown in Fig. 71(*b*). We may consider first the relation between the energy E and the wave number k. If the potential were uniform, these would be related by the simple equation V (4), so that the curve connecting E and k would be of the form shown in Fig. 73(*a*). In the presence of a periodic potential, the corresponding curve is of the type shown in Fig. 73(*b*), where the vertical portions a_1b_1, a_2b_2, . . . represent the forbidden ranges of energy. If electrons are introduced with continually increas-

ing values of k, then when k reaches the critical value corresponding to a_1, there is an abrupt increase in the energy on passing to the next highest wave number k. The lowest portion of the curve in Fig. 73(b) closely resembles that of the free-electron curve of Fig. 73(a), so that on introducing electrons into the one-dimensional model with periodic potential, the first electrons behave very like those of the free-electron model; but at the higher energies there is a series of breaks in the curve, and near to these the behaviour is very different. Each portion of the curve in Fig. 73(b) may be called a band, and the curves are horizontal at the top and bottom of each band. Near to the bottom of each band the curves are parabolic if the energy is measured from the bottom of the band, and the curves are also parabolic at the top of a band, with the curvature in the opposite direction. The curves are of such a nature that d^2E/dk^2 is positive in the lower portion of a band and negative at the upper portion. These general characteristics apply to all regular periodic variations of potential, but the exact assumptions made determine the magnitudes of the energy gaps a_1b_1, a_2b_2, &c., and affect also the finer details of Fig. 73(b), such as the exact positions of the points a_1b_1 relative to the simple curve of Fig. 73(a).

We may now turn to a three-dimensional crystal structure, and if Fig. 72 represents the three-dimensional k-space, and we consider any line such as OA, then the passage from O to A represents a series of electron states with increasing values of k, all referring to the same direction of the wave motion.* If we confine our attention to those energy states whose wave numbers lie along any one direction such as OA, the theory indicates that the relation between the energy E and the wave number k is given by a curve of the same general form as that in Fig. 73(b), so that as k increases there are breaks in the curve corresponding to forbidden ranges of energy. The positions at which the breaks occur depend on the direction considered. If, therefore, we consider the position of the gap a_1b_1 at the top of the first band, this will depend on the direction, and there will be a series of curves such as those shown in Fig. 74, where each broken curve such as Oa_1b_1c refers to one direction in k-space. In general, these curves are not horizontal at points such as a_1 or b_1, but for some directions they are horizontal (see p. 191). Exactly similar considerations apply to the positions of the energy gaps at the top of the later bands, and these again vary with the direction considered. It is customary to represent the positions of these breaks for the different directions by means of a surface in a three-dimensional diagram with k_x, k_y, and k_z as axes.

* As explained above, although the individual states at A correspond with motion in the direction OA, they combine together to form a wave group which in general does not move in the direction OA.

These surfaces have the characteristic that they are composed of a number of planes which build up the so-called *Brillouin Zones*, and the limit of the occupied states may be indicated by a ruled surface within the zone. Figs. 75(*a*) and (*b*) show the first Brillouin zone for the face-centred cubic structure. The meaning of these diagrams is that if we start at the origin of k-space, and consider a series of states with continually increasing k, then E varies continuously with k as long as k lies within the zone; but when k reaches the surface of the zone, there is an abrupt increase in E, corresponding to the gaps a_1b_1, a_2b_2, . . . &c., in Fig. 74. In Fig. 75(*a*), the number of electrons

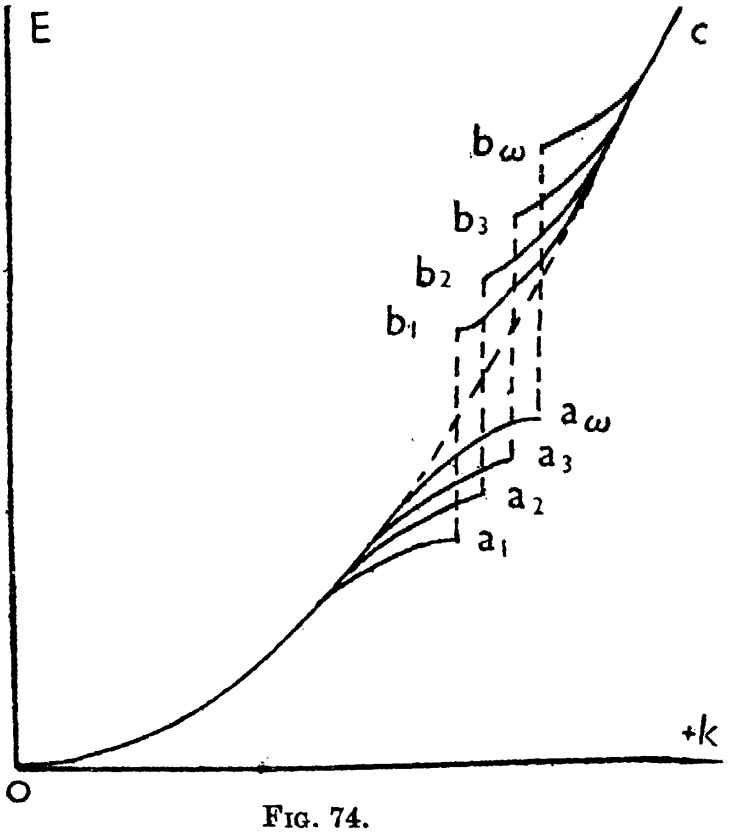
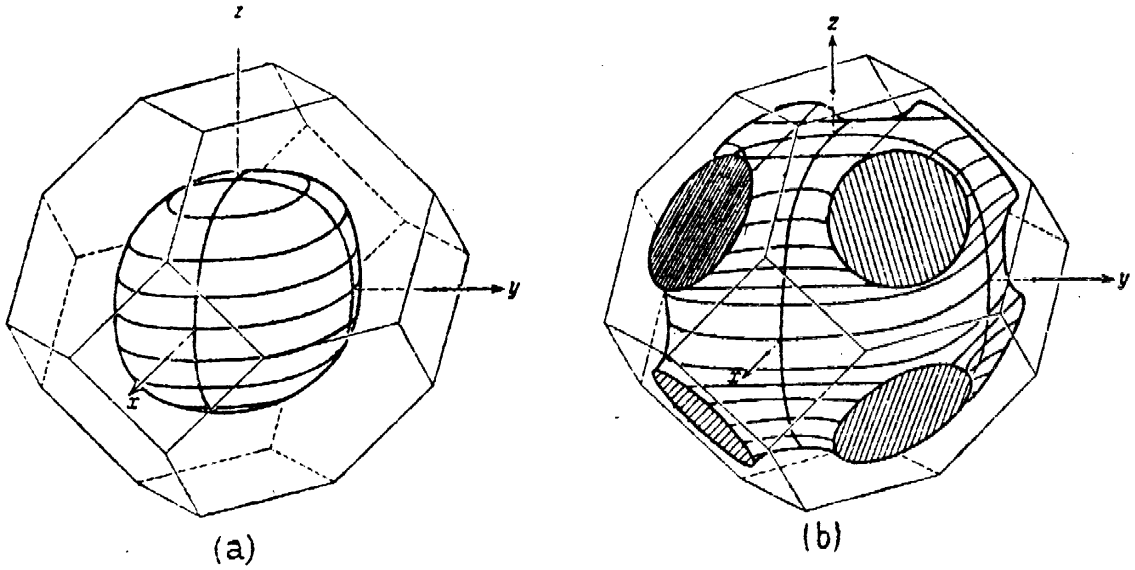


FIG. 74.

per atom is assumed to be relatively small, so that the occupied states contained within the ruled surface lie well within the zone boundaries; this corresponds to the condition of affairs in a univalent metal. In Fig. 75(*b*) the number of electrons per atom is sufficiently great for the occupied states to have reached the surface of the zone, and the abrupt increases in energy at the zone surfaces prevent electrons from entering the next states in the directions concerned. Diagrams such as Fig. 75 do not give the magnitude of the energy gaps at different points on the surface of the zone, but they show clearly the dependence on direction of the points at which the breaks occur in the curves of Fig. 74. If the value of k at which the energy gaps occurred were

independent of direction, the Brillouin zone would be a sphere, but as we shall see later the shapes of the Brillouin zones for some crystal structures are very different. It will be seen, therefore, that there is an essential difference between the E/k relations in the free-electron theory and in the theory of the periodic field. In the free-electron theory, for all directions of wave number, E increases continuously



[*Courtesy Clarendon Press.*

FIG. 75.—The First Brillouin Zone of the Face-Centred Cubic Structure. The zone is bounded by planes parallel to the cube and octahedral faces. Within the zone the energy varies continuously with the wave number, but on reaching the zone face there is an abrupt increase in energy on passing into the next zone. In Fig. 75(*a*) the number of electrons per atom is small, and the ruled surface shows the limit of the occupied states; this corresponds with the condition of affairs in a univalent metal, and it will be seen that the ruled surface is nearly spherical. The ruled surface is a surface of constant energy (see p. 181), and, as explained on pp. 181 and 194, the direction of motion of an electron in a group of states on the ruled surface will be perpendicular to the ruled surface at the place considered. In Fig. 75(*b*) the number of electrons is greater, and the Fermi surface of occupied states has reached the zone boundary. It will be seen that near the zone boundaries the ruled surface of constant energy is very different from a sphere, and bends round so as to be perpendicular to the zone faces at the points where they meet the ruled surface. This is an expression of the fact described on p. 189 that for electron states on the zone surface the component of velocity of the electron perpendicular to the zone face is zero.

with k, and as electrons are introduced into the box model, the energy increases smoothly and continuously. In the theory of the periodic field, for each direction of the wave number there is a series of breaks in the E/k curve, and the values of k at which these breaks occur lie on the surfaces of the Brillouin zones.

In considering a Brillouin zone such as that of Fig. 75 two possibilities arise. In the first case, which is that illustrated in Fig. 74, the energies of states at the top of the first band may *for all directions*

be less than the energy of any state for any direction at the bottom of the second band. In this case, if we introduce increasing numbers of electrons into the crystal,* the first electrons will fill up the states in k-space almost as in the free-electron model, the Fermi surface (see p. 181) will be almost spherical, and the $N(E)$ curve (see p. 157) will be parabolic as in the free-electron model. With increasing numbers of electrons the values of k for the highest occupied states will begin to approach the surface of the zone in certain directions, and when the surface of the zone is reached, it will no longer be possible to add electrons whose states are in the directions concerned, since this would involve an abrupt increase in energy. When this stage is reached, the $N(E)$ curve will show a sharp fall, because there will no longer be possible energy states for some directions of the wave number. The resulting $N(E)$ curve is of the form shown in Fig. 76(b), the point a_1 representing the stage at which the surface of the zone is first touched,

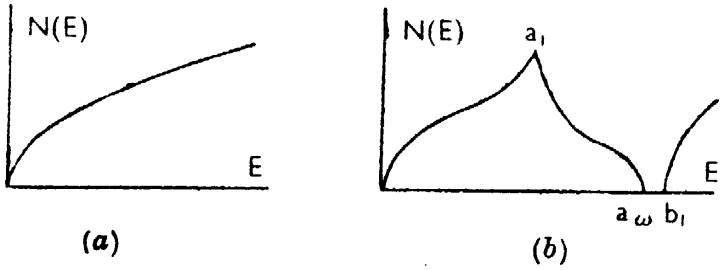


FIG. 76(a) shows the form of the $N(E)$ curve in the free-electron theory; here $N(E) \propto E^{\frac{1}{2}}$.

FIG. 76(b) shows the corresponding curve in the Brillouin-zone theories; the example is one in which the first and second zones do not overlap.

corresponding with the point a_1 on the lowest curve of Fig. 74. It will be noted that just before a_1 the $N(E)$ curve rises above that for the free-electron model, and here the Fermi surface is no longer spherical. On adding still more electrons, the values of k increase, and more and more directions are affected, until eventually all the states in the first Brillouin zone are occupied; at the same time the $N(E)$ curve sinks to zero, as shown in Fig. 76(b), where the point a_ω represents the top of the last curve for the first band in Fig. 74. When the first Brillouin zone is filled, the next electron state will involve a sudden increase in the energy, this increase being equal to the difference between the energies of the point b_1, representing the lowest energy of the group

* When we speak of introducing increasing numbers of electrons into the crystal it is, of course, always assumed that a corresponding positive charge is present, so that the whole is electrically neutral. In actual alloys, the most usual way of changing the electron concentration is to alloy a given metal with another which forms a simple primary solid solution, but is of different valency. In this way the number of valency electrons per atom is changed, but the structure is unaltered.

of curves for the second band in Fig. 74, and the point a_ω at the top of the highest curve of the first band. The second and third Brillouin zones may be separated in the same way, so that on introducing increasing numbers of electrons the second zone is completely filled before any electrons enter states in the third zone.

In the second case, the curves of Fig. 74 may be so related that, although for any one direction there is an energy gap at the top of the first band, some of the states at the bottom of the second band have lower energies than the highest states at the top of the first band. This condition of affairs is shown in Fig. 77, and the resulting

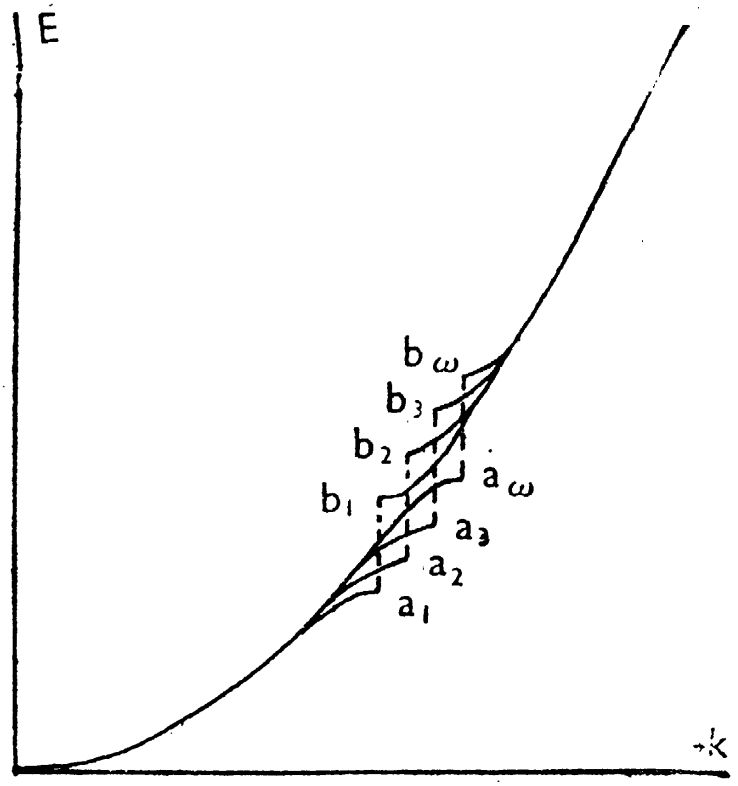


FIG. 77.

$N(E)$ curve in Fig. 78. In this case, on adding increasing numbers of electrons to the crystal, the first electrons enter the first Brillouin zone, as in the preceding case, and the $N(E)$ curve is of the form shown in Fig. 78, the sharp fall at a_1 corresponding with the stage at which the Fermi surface of occupied states first touches the surface of the first Brillouin zone, *i.e.*, the point a_1 on the lowest curve in Fig. 77. The point b_1 in Fig. 78 represents the stage at which the electrons begin to enter the second Brillouin zone, and corresponds with point b_1 on the lowest curve of the second zone in Fig. 77. At this stage the states in the first zone are not completely filled, because the energy of the point a_ω on the highest of the curves for the first zone in Fig. 77 is

greater than the energy for the point b_1. As more electrons are added, they enter the remaining states of the first zone and the lowest states of the second zone, and the resulting $N(E)$ curve in Fig. 78 is given by the sum of the ordinates for the two zones where these overlap. The sudden rise in the $N(E)$ curve after b_1 is the result of the opening up of a series of new states when the second zone is entered. Finally, the point a_ω represents the stage at which the first zone is completely filled, and further electrons continue to fill up the second zone. With increasing numbers of electrons, a second peak occurs when the Fermi surface reaches the surface of the second Brillouin zone, and a second kink in the curve occurs if the second zone overlaps the third. Later zones produce similar effects, and, if the zones overlap, the typical $N(E)$ curve shows a whole series of peaks and valleys, the positions of which depend upon the crystal structure, and on the magnitude of the energy gaps at the surface of a zone. Some of the more interesting of these curves are discussed in Part VI.

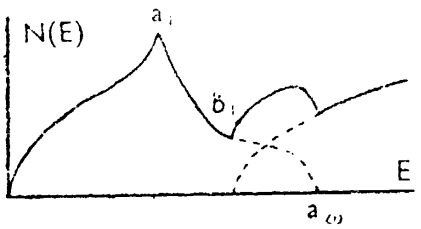


FIG. 78.

The cyclic model is able to deal with problems involving a flow of electrons in a definite direction, and, as in the free-electron theory, the moving electron must be thought of as a wave packet, which travels with the group velocity v. We may deal first with the one-dimensional model referred to on p. 182. The group velocity v is given by :

$$v = \frac{d\nu}{d\left(\frac{1}{\lambda}\right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{V (6)}$$

which for electron waves is equivalent to :

$$v = \frac{2\pi}{h}\frac{dE}{dk} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{V (7)}$$

From the form of the curves in Fig. 73(*b*), it follows that the group velocity is zero for electrons at the top and bottom of each band. In the free-electron theory, increasing wave number or increasing energy means a continually increasing velocity, but in the periodic field this is no longer so, and, on starting from the bottom of the first band, increasing energy first results in an increase in v, but as the top of the band is approached dE/dk diminishes, and eventually becomes zero where the curve is horizontal at the point a_1 in Fig. 73(*b*). The energies in the range a_1b_1 are forbidden energies, and on reaching b_1 in the second band the velocity is zero; on passing up the second band the

velocity, v, at first increases and then decreases. The relation between velocity and wave number is thus one in which the velocity in each band is zero at the bottom of the band, rises to a maximum, and then sinks to zero at the top of the band.

The fact that the velocity, v, is zero at points such as a_1 and b_1 in Fig. 73(b) is not to be taken as implying that the electron is at rest. The wave functions at points such as a_1 and b_1 represent standing waves, but since the group velocity of the wave packet is zero, these standing waves cannot be interpreted as representing equal probabilities of the electrons moving in opposite directions up and down the length L of the one-dimensional model, as was the case for the standing waves in the box model of the free-electron theory. In the periodic field, the standing waves at points such as a_1 and b_1 in Fig. 73(b) may still be regarded as indicating an equal probability of finding the electron moving in opposite directions, but since the velocity of the wave packet as a whole is zero, the process concerned is within the length of the wave packet, and cannot therefore be visualized in the form of a definite trajectory. Strictly speaking, we cannot do more than say that the velocity of the wave packets is zero for electrons in states such as a_1 and b_1 of Fig. 73(b). If we try to look into the process further, however, we may perhaps say that the velocity $v = 0$ is to be interpreted as an equal probability of finding the electron moving in opposite directions, so that the electron is travelling first in one direction and then in the opposite direction; but these reversals of motion occur within the length of the wave packet, so that we cannot visualize the process or draw a definite trajectory. The energy of electrons in these states is thus neither entirely potential energy, nor to be visualized as the kinetic energy of long-range translatory motion, but is in a form which is characteristic of the wave-mechanical behaviour of an electron in a periodic field.

We may now turn to the three-dimensional model for which the relation between energy and wave number is of the form shown in Fig. 74, where each curve refers to one direction of wave number, and the breaks in the different curves occur at the values of k which lie on the surface of a Brillouin zone, such as of Fig. 75. The velocity of an electron can be resolved into components parallel and perpendicular to the surface of a zone,* and the picture presented is that an electron in a state on the surface of a zone has a zero component of velocity in a direction perpendicular to the surface concerned. The

* The Brillouin zones are, of course, in k-space, but since the axes k_x, k_y, k_z in Fig. 73 represent motion parallel to the x, y, z axes, it is customary to speak of motion parallel and perpendicular to the surface of a zone.

physical process associated with this is that the electron has a wave-length such that it undergoes a Bragg reflection within the crystal. Let us suppose, for example, that Fig. 79 shows parallel planes of atoms within the crystal, and that we allow a monochromatic beam of electrons travelling in the direction AB to impinge on the crystal from outside. Then, in general, an electron with wave number k, corresponding to motion in this direction, will be transmitted with comparatively little scattering. If, however, we consider a series of electrons with increasing k, a stage will be reached at which the wave-length satisfies the Bragg equation :

$$n\lambda = 2d \sin \theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{V (8)}$$

and then strong reflection takes place so that the electrons do not penetrate far into the lattice. During this reflection, the component of velocity parallel to the reflecting plane is unaltered, whilst the component perpendicular to the reflecting plane is reversed in direction. We can thus understand why a difference exists between the behaviour of electrons in the free-electron model, and in the periodic field of a lattice. In the free-electron model, the introduction of electrons with increasing wave numbers can take place as a continuous process, but in the lattice the wave-like characteristics of an electron mean that for each direction of the wave number there will be certain critical points at which the condition for a Bragg reflection is satisfied. It is these critical wave-lengths which correspond with the electron states on the surface of a Brillouin zone. We have already explained that electrons in these states have a zero component of velocity perpendicular to the face of the zone concerned, and if we are asked what picture we can give of the motion inside a crystal of an electron whose wave number lies on the surface of a Brillouin zone, we may perhaps answer that, since in a Bragg reflection the angle of incidence is equal to the angle of reflection, the electron may be regarded as undergoing repeated Bragg reflections inside the crystal, so that the mean component of velocity perpendicular to the zone face is zero, but successive reflections occur within the length of the wave packet, and consequently we cannot draw a definite trajectory or form any picture of the process in terms of the classical mechanics of " ordinary particles."

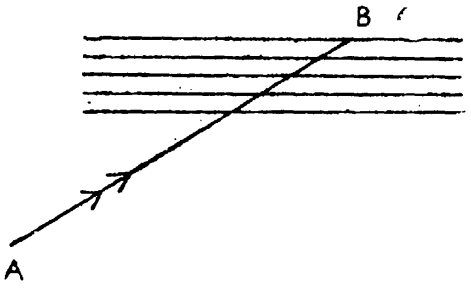


FIG. 79.

From the above description it will be appreciated that since the

corner of a zone involves the intersection of at least three planes, the mean velocity associated with an electron state whose wave number lies at the corner of a zone, is zero, although as in the one-dimensional case discussed above, this is to be interpreted not as a stationary electron, but as equal probabilities of motion in opposite directions, the reversals of motion occurring within the length of a wave packet, so that no definite picture can be formed.

The above considerations indicate clearly that there is an intimate relation between the shapes of the Brillouin zones and the X-ray or electron-diffraction patterns characteristic of the structure concerned. Thus, the first Brillouin zone shown in Fig. 75 for the face-centred cubic structure is bounded by octahedral planes, cut off by planes parallel to the faces of the cube, and this corresponds with the fact that the first two strong reflections for the face-centred cubic structure are those from the (111) octahedral and (200) cubic sets of planes. This correspondence is the foundation of many of the methods for obtaining the shapes of the Brillouin zones of the different structures, but these lie outside the scope of the present work.

For an electron state at the surface of a Brillouin zone, the mean velocity v associated with the state has a component perpendicular to the zone face equal to zero. From this it will be appreciated that if we consider the relation between E and k for states along one direction of k-space, such as the line OA in Fig. 72, then the curves in Figs. 74 and 77 will be horizontal at the points a and b if OA in Fig. 72 is perpendicular to a zone face, or if OA passes through the corner of a zone. In the general case, however, the curves will not be horizontal, because although the component of v perpendicular to the zone face vanishes, the component parallel to the zone face is unaffected.

In the above description (p. 186) of Fig. 76(b) we have assumed that the first Brillouin zone is bounded by faces of one type only, the point a_1 representing the stage at which the Fermi surface of occupied states first touches the faces of the zone, all of which are at the same distance from the origin. In many cases, the first zone is bounded by faces of more than one type. Thus, as shown in Fig. 75, the first zone for the face-centred cubic structure is bounded by a combination of octahedral and cube faces, and these lie at different distances from the origin. In this case the $N(E)$ curve will rise to a first peak at the stage where the Fermi surface first touches the octahedral faces of the zone, and will then fall and rise to a second peak when the Fermi surface first touches the cube faces of the zone (these two peaks are marked A and B in Fig. 114, p. 252). In the general case, therefore, the $N(E)$ curve for the first zone contains more than one peak.

SUGGESTIONS FOR FURTHER READING.

N. F. Mott and H. Jones, "The Theory of the Properties of Metals and Alloys." Oxford: **1936** (Clarendon Press).

A. Sommerfeld and H. Bethe, "Elektronentheorie der Metalle." (Handbuch der Physik. Zweite Auflage. Band XXIV. Zweiter Teil.) Berlin.

F. Seitz, "The Modern Theory of Solids." New York: **1940** (McGraw-Hill Book Co., Inc.).

Chapter XXIV.—Insulators, Semi-Conductors, and Metals.

Before dealing with the more complete theories of Brillouin zones, we shall describe the general bearing of this kind of theory upon the problem of electrical conductivity, since this can be understood in terms of the simple zone theories. From the point of view of electrical conduction, substances may be divided into the following main classes: insulators, semi-conductors, electronic conductors, and electrolytic conductors. The last of these will not be considered here, since they are seldom met with in the study of solid metals and alloys, although it should be noted that if the constituent elements differ greatly in their electrochemical nature, a certain amount of electrolytic conduction may take place when an electric current is passed through a liquid alloy. It is one of the great triumphs of the Bloch theory that it is able to give a satisfactory explanation of the remaining three classes of substance, and in particular to explain the enormous difference between the electrical resistance of a substance such as a diamond and that of a metal. Differences in the strengths of the binding forces between electrons and atoms might affect the resistance by a factor of 10 or 100, but the actual resistance of the diamond is so great that some entirely new factor must be at work, and the Brillouin-zone theory provides the required explanation.

In the description of the simple free-electron theory, we saw how, in the absence of an electric field, the velocity distribution of the electrons was perfectly symmetrical, so that no resultant flow occurred in any one direction, whilst in the presence of a field, a slight displacement of the velocity distribution took place, until a steady state was set up in which the acceleration of the electrons in the direction of the field was counterbalanced by the collisions with the atoms, or more properly the thermal vibrations of the lattice. In the zone theories, the same line of approach may be used, but the conclusions are very different owing to the ranges of forbidden energy which correspond with wave numbers k on the surfaces of the Brillouin zones. We may note first that wave mechanics indicates that an electron can move freely and without resistance in a perfectly periodic field, and in this way the very long free paths indicated by experiment can be understood.

We may begin first by considering the behaviour of one single electron in a periodic field, and for simplicity in drawing we may consider a hypothetical two-dimensional solid with a periodic field for which the first Brillouin zone is a square, as shown in Fig. 80.

Let us suppose that the electron is in the state represented by the point P. If the energy contours are circles, the velocity of the electron will then be in the direction OP, whilst if the energy contours are of a different form the velocity of the electron will be perpendicular to the contour at the value of k concerned. We may now suppose that an electric field is applied in the direction shown. In the presence of the

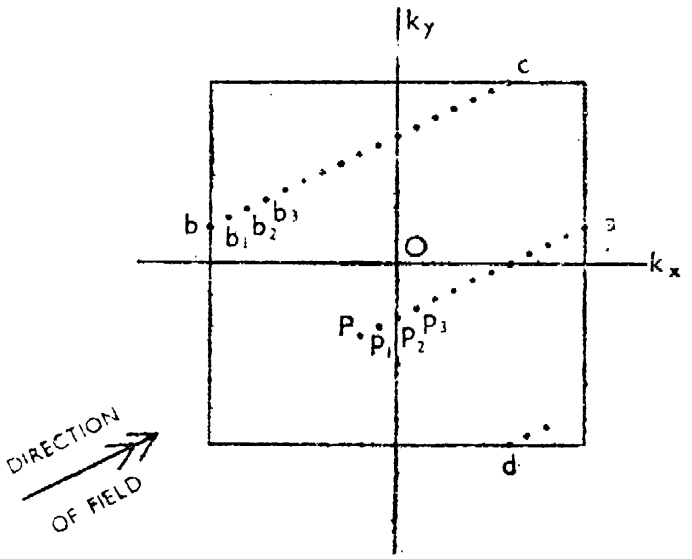


FIG. 80.

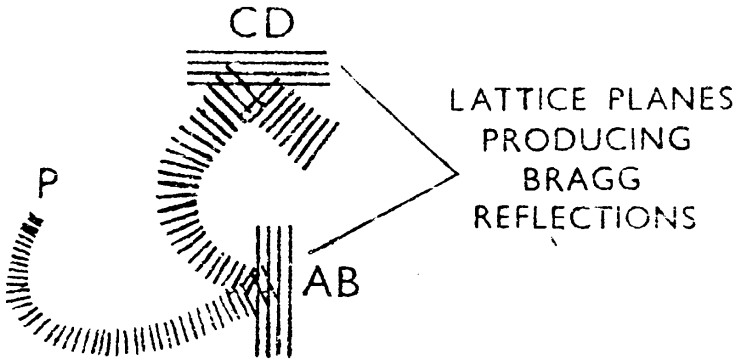


FIG. 81.

field the wave number of the electron tends to increase in the direction of the field, and the effect of the field is to make the electron pass through a series of states p_1, p_2, p_3, . . . until the zone boundary is reached, and a break occurs in the E/k curve. Calculation then shows that even if the gap in the energy curve is quite small, say 1 e.v., the probability of the electron passing to a state in the next zone is very small. On reaching the state a in Fig. 80 the electron, therefore, does not pass into a state in the next zone, but undergoes a Bragg reflection

in the lattice, as a result of which the component of velocity perpendicular to the zone face is reversed, and the electron state jumps from the point a to the point b in k-space. Under the influence of the electric field, the electron then passes through a succession of states b_1, b_2, b_3, . . . until it reaches the point c on the surface of the zone, when a Bragg reflection again occurs and the electron jumps from the state c to the state d, and a similar sequence of changes then takes place. The general effect of an electric field is thus to make the wave number k change continuously in the direction of the field until the wave number k reaches a state on the surface of the Brillouin zone where an energy gap occurs; at this stage there is an abrupt change in k, corresponding to a Bragg reflection in the lattice.

Fig. 80 shows the way in which the wave number k changes under the influence of an electric field. The velocity, v, of the electron is proportional to dE/dk (see p. 188), and as long as the energy contours are spherical, v and k are in the same direction, since v is perpendicular to the energy contour (see p. 181). It follows, therefore, that so long as the energy contours are spherical, the effect of the electric field is to change v and k in the same way, and the electron is accelerated in the direction of the field. Where the energy contours are no longer spherical, the effect of the electric field is to change k in the direction of the field, as shown in Fig. 80, and as k passes through the succession of points p_1, p_2, p_3, . . ., the velocity, v, changes so that it is perpendicular to the energy contours at the succession of points p_1, p_2, p_3. . . . It follows, therefore, that as the wave number k approaches the surface of the zone, where the energy contours are no longer spherical, and v and k are not in the same direction, the velocity of the electron, v, will no longer be changed in the direction of the field, and the acceleration of the wave packet which represents the electron will no longer be in the direction of the force. It is thus important to recognize that near to the surface of a zone, it is k and not v, which changes in the direction of the applied field. This is an example of the point previously emphasized (p. 180) that the individual waves moving in one direction may build up a wave group moving in another direction.

Fig. 80 shows the way in which the points representing the states of an electron change under the influence of an electric field. If we are asked what path the electron follows, it will be appreciated that from Heisenberg's Principle we cannot follow the electron in detail along its path, but we may obtain a general idea of the process involved as follows. We may regard the velocity as resolved into components parallel and perpendicular to the field, and for simplicity we may assume that the energy contours are everywhere spherical, so that we

ignore the complications near to the zone boundaries. We may then say that the general effect of the electric field is to accelerate the component of velocity parallel to the field, and to leave the perpendicular component unchanged. We may suppose that when the electron state is near the point P in Fig. 80, the electron itself is somewhere near a point P in real space, as shown in Fig. 81. Then by Heisenberg's Principle there will be a mutual uncertainty in our knowledge of the wave number and the position, and we may represent this by a shaded area in Fig. 81. Since we are assuming the energy contours to be spherical, the velocity of the electron in the states P, p_1, p_2, p_3, . . . in Fig. 81 will be in the directions OP, Op_1, Op_2, Op_3 . . . and the passage of the electron along the series of states p_1, p_2, p_3, . . . in Fig. 80 will correspond to a curved trajectory in which the position becomes more and more uncertain as the wave packet spreads out. This curved trajectory is shown as a shaded region PAB in Fig. 81 in order to emphasize the uncertainty in the simultaneous position and wave number of the electron. At the point AB the wave number has reached the critical value for a Bragg reflection from the planes of atoms parallel to the side of the square lattice in Fig. 81, and the reflection takes place as shown, so that the angle of incidence equals the angle of reflection, and the electron jumps from state a to b in Fig. 80. The electron then sets out on a new curved trajectory as shown. This description is, of course, very greatly over-simplified, and in the neighbourhood of the zone boundaries the energy contours are distorted, with the result that the force and the acceleration of the wave packet may no longer be in the same direction. The general process described above does, however, still take place, and the effect of an electric field on a single electron in a periodic field is to make the electron undergo a series of curved paths terminated by Bragg reflections. It should be emphasized that these Bragg reflections take place at the absolute zero of temperature, and are quite distinct from the scattering of the electrons by "collisions" with the thermal vibrations of the lattice, which give rise to the resistance at temperatures above the absolute zero.

From the above description it will be appreciated that if there is an energy gap at the surface of a zone, an external electric field * will not enable an electron to pass from a state in one zone to a state in another. It follows, therefore, that at the absolute zero a substance must be an insulator if the number of valency electrons per atom completely fills a Brillouin zone with an energy gap across all of its

* In the whole of the present description we are ignoring the use of the very high voltages which cause the breakdown of an insulator.

surfaces (Fig. 76(*b*)). In such a case, the application of an electric field can produce no resultant flow in any direction, because, since electrons are indistinguishable and all the states in the zone are occupied, no interchange of electrons among these states can affect the distribution of the assembly as a whole. In so far as it is justifiable to consider the individual electron under these conditions, we may imagine each electron to undergo paths of the general type shown in Fig. 81, subject to the conditions that an electron can only enter a state which has been vacated by another, and since the Bragg reflections prevent transitions to states outside the zone, and all the states within the zone are occupied, the electric field can produce no effect on the distribution as a whole.

The above remarks refer to the effect of an electric field at the absolute zero of temperature and in the absence of other complicating factors, and they show that an insulator is essentially a structure in which the number of electrons is sufficient to fill one or more Brillouin zones, the outermost of which is completely separated from the next zone, as in Fig. 76(*b*). If, however, the insulating crystal is illuminated by light of sufficiently short wave-length, electrons may be excited photoelectrically from the full zone to a higher zone, where they will be free to act as conduction electrons, and in this case the phenomenon of *photoconductivity* is shown. It is important to note that the excitation of the electron into the higher zone which produces the conductivity is due, not to the effect of the applied electric field, but to the absorption of the quantum of light. In the same way, if the energy gap at the surface of the filled zone is not too great, rise of temperature may result in the thermal excitation of electrons into the next zone, where they will be free to act as conduction electrons. This effect is discussed later (p. 206) in connection with semi-conductors.

It is, of course, well known that many insulating substances such as the diamond, can be regarded as co-valent structures in which each atom satisfies its normal valency by sharing electrons with $(8-N)$ neighbours, where N is a number of the group to which the element belongs (p. 100). In the diamond structure, for example, each atom has four close neighbours, and the whole crystal may be regarded as a gigantic molecule in which the atoms satisfy their normal valencies. If it is asked how this conception affects the picture presented by the Brillouin-zone theories, the answer is that each represents part of the truth. The co-valency theory emphasizes that the electron-cloud density of the valency electron is greatest round the lines joining a given atom to its four neighbours. The Brillouin-zone theory emphasizes that the valency electrons belong to, and are free to move

within, the crystal as a whole, but does not deal with the variation of the electron-cloud density in space. Each theory, therefore, represents part of the truth, and the two are complementary and not antagonistic to one another.

We may now consider structures in which the number of valency electrons per atom is small compared with that required to fill a zone. In all simple translational lattices, each Brillouin zone contains $2N$ electron states, where N is the number of atoms in the crystal. It follows, therefore, that in the univalent alkali metals, and copper, silver, and gold, the occupied states only take up one-half of the first Brillouin zone. Fig. 75(*a*) shows the first Brillouin zone for the face-centred cubic structure (copper, silver, and gold), and the Fermi surface is drawn so as to show the limits of the states occupied with one valency electron per atom. It will be seen that the Fermi surface is a slightly distorted sphere, and that there are unoccupied states on all sides of those which are occupied.

Under these conditions the picture of electrical conductivity is very like that previously described for the simple free-electron model. In the absence of an electric field, the velocity distribution is symmetrical, so that for each electron with velocity $+ v$, there is one with velocity $- v$, and the total flow of electricity in any one direction is zero. In the presence of an electric field, there is a slight shift in the velocity distribution, giving rise to a resultant current in the direction of the field, and a steady state is set up in which the effect of the field is neutralized by the collisions with the thermal vibrations of the lattice. The picture is complicated by the fact that if an electron escapes collision for a time sufficient to enable its wave number, under the influence of the electric field, to reach the surface of the Brillouin zone, then a Bragg reflection takes place just as was described in connection with Figs. 80 and 81. If the electron concentration, *i.e.*, the number of valency electrons per atom, is greater than one,* the Fermi surface spreads out until it touches the surface of the zone, as shown in Fig. 75(*b*), and under these conditions Bragg reflections are naturally more common.

We have already seen that although in some structures the different zones are completely separated (Figs. 74 and 76), there are others in which the overlapping of the zones takes place (Figs. 77 and 78). This latter case of overlapping zones is characteristic of most, if not all, structures with normal metallic properties. If the electron concen-

* Thus, in silver–aluminium alloys, the α-solid solution in silver can contain as much as 20·4 at.-% of aluminium, and the electron concentration may be as great as 1·408, since each aluminium atom contributes 3 valency electrons.

tration is small compared with that required to fill the first zone completely, the condition of affairs will be as shown in Fig. 82(*a*), where the shaded area represents the limit of the occupied states; this corresponds with Fig. 75(*a*), discussed above. If, on the other hand, the electron concentration were greater, the condition of affairs might be as shown in Fig. 82(*b*), where the whole of the states in the first zone, and some of those in the second zone, are occupied. In such a case, the electrons in the first zone do not contribute to the electrical conductivity. If the zone characteristics are such that in any given direction there is a break in the E–k curve, the external electric field will not enable an electron in the first zone to leave that zone, because when k reaches the surface of the zone, a Bragg reflection takes place. The electrons in the first zone thus form a group of electrons, which, although free to move, do not produce a resultant flow in any direction. It must not, however, be imagined that a given electron which is in the first zone at one instant remains in this zone indefinitely. At finite temperatures there is always a certain probability of an electron

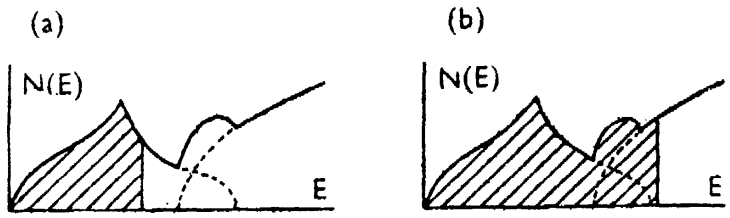


FIG. 82.

passing from the first to the second zone as the result of thermal excitation, this probability increasing with rise of temperature. Mere acceleration under the action of an electric field only gives a very small probability of the electron passing from one zone to another if there is an energy gap at the surface. There are, however, some metallic structures with overlapping zones (*e.g.*, the close-packed hexagonal) in which, although there is an energy gap at the surface of the zone, this energy difference becomes zero along some of the edges of the zone (see p. 241), and in such cases the application of an electric field in certain directions relative to the crystal axes may enable an electron to pass through a series of states beginning in one zone and ending in another.

The above considerations serve to emphasize that although all the electrons take part in the process, the number effective in producing conductivity does not necessarily increase with the number of electrons per atom. Thus, in the case of Fig. 82(*b*), the electrons which occupy the first Brillouin zone can contribute nothing to the conductivity,

and there are fewer electrons contributing to the conductivity than in the case of Fig. 82(*a*), although the number of valency electrons per atom is greater for the case of Fig. 82(*b*).

To describe the conductivity process further we may for simplicity use a two-dimensional model in which the first Brillouin zone is a square. Fig. 83(*a*) shows a case in which there are relatively few electrons per atom, and the occupied states are represented by the shaded circle, the circumference of which corresponds to the surface of the Fermi sphere in the three-dimensional model. Under these conditions the picture of conductivity is very like that of the free-

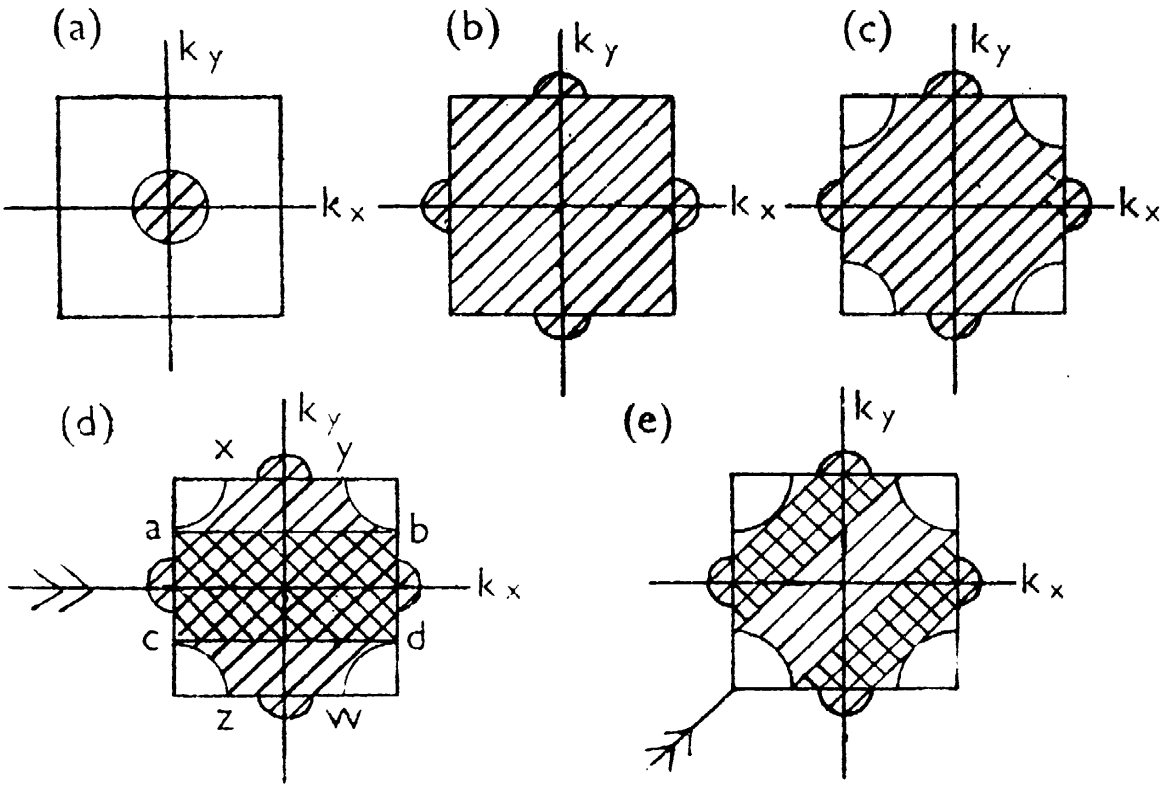


FIG. 83.

electron model (p. 170); all of the electrons take part in the conductivity process, but only those at the edge of the circle can give a resultant flow in any one direction, or undergo collisions which affect the velocity distribution.

Fig. 83(*b*) shows a case in which the first zone is completely filled and there is an overlap into the second zone. Here, in the general case,* only the electrons in the second zone produce a conductivity, and the position is analogous to that of Fig. 82(*b*).

Fig. 83(*c*) shows a case in which the overlap into the second zone

* As explained before (p. 198), in some structures the energy gaps may vanish at certain points on the zone surface.

has begun before the first zone is completely filled. The occupied states are shown by single shading, and the corresponding $N(E)$ curve is shown in Fig. 84. We may now consider the effect of the application of an electric field from left to right as in Fig. 83(*d*). In such a case the group of electrons whose states are within the rectangle *abcd*, which is shown in double shading, cannot contribute to a conductivity in the direction of the field, because for each state of $+k$ there is one of $-k$, and in the general case the energy gaps at the boundaries of the zone prevent the electrons from passing to a state lying outside the zone. The group of electrons whose states lie in the areas *axyb* and *czwd* of the first zone, and those in the second zone can, however, undergo a displacement of the velocity distribution so as to produce a resultant flow in the direction of the field, although, as will be appreciated from p. 170, it is only those electrons in states near the Fermi surface which are really effective in determining the conductivity. If, for example, velocities are referred to the direction of the field, then for each electron whose state is near the centre of the area *axby* of Fig. 83(*d*) and which corresponds to a velocity $+v$, there is one with a velocity $-v$, and so it is only electrons near the Fermi surface which can contribute to the conductivity. On the other hand, the group of electrons with states inside the area *abcd* of Fig. 83(*d*) cannot give rise to a resultant flow at all. If the applied field had been in the direction of the diagonal of the square, as shown in Fig. 83(*e*), then the group of electrons whose states are shown by the doubly shaded areas would be those which did not contribute to the conductivity.

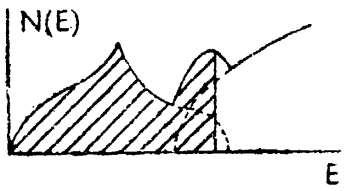


FIG. 84.

From the preceding description it will have been realized that the electrons at the bottom of the first zone behave very like those of the free-electron theory, and the same applies to electrons at the bottom of higher zones, *provided that the energy is reckoned from the bottom of the zone concerned.* Thus, the $N(E)$ curves of the second zones in Figs. 76(*b*) and 78 are parabolas of the form $N(E) \propto (E-E')^{\frac{1}{2}}$, where E' is the energy at the bottom of the second zone. In general, for the few electrons in states at the bottom of zones, the relations between energy and other properties (*e.g.*, wave number, velocity v, $N(E)$) are similar to those of the free-electron model, provided that the energy is measured from the bottom of the zone concerned.

At the top of the zone the position is very different, and some of these complications may now be described. We have seen before

(p. 188) that for the one-dimensional model, the group velocity v is given by :

$$v = \frac{2\pi}{h} \cdot \frac{dE}{dk} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{V (9)}$$

Under the influence of an electric field, the wave number, k, in the direction of the field increases uniformly with time, and the variation is given by the equation :

$$\frac{dk}{dt} = \frac{2\pi eF}{h} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{V (10)}$$

It follows, therefore, that the rate of change of the group velocity is given by :

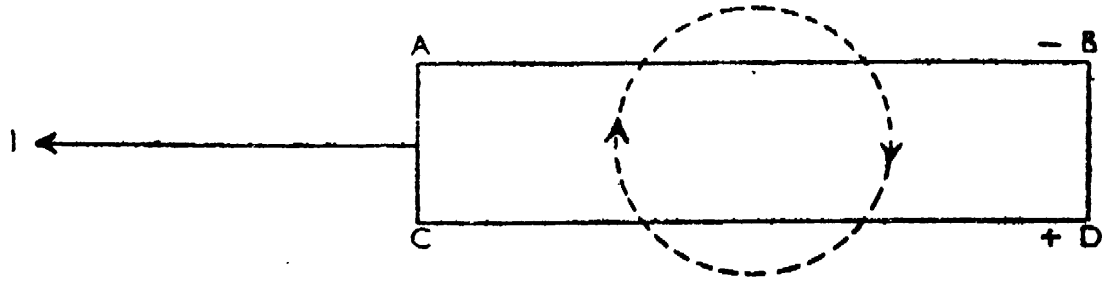
$$\frac{dv}{dt} = \frac{2\pi}{h} \cdot \frac{d}{dt}\left(\frac{dE}{dk}\right) = \frac{d^2E}{dk^2} \cdot \frac{4\pi^2}{h^2} \cdot eF \quad . \quad . \quad . \quad \text{V (11)}$$

If this is compared with the classical expression, eF/m, for the acceleration, it will be seen that the mass m is replaced by the expression :

$$\frac{h^2}{4\pi^2 \dfrac{d^2E}{dk^2}}$$

and it is customary to call this last quantity the *effective mass* of the electron, and the symbol m^* is sometimes used to denote this quantity. Examination of equation V (11) leads to interesting conclusions, for it will be seen that when d^2E/dk^2 is negative, the acceleration is negative. Examination of Figs. 73(*b*) and 74 will show that d^2E/dk^2 is negative for states in the upper portion of a band, and consequently for electrons in these states the effect of an electric field is to diminish the group velocity, v, and the effect is in some ways as though the electron had a negative mass. This is a characteristic of the behaviour of electron wave packets in a periodic field, and it is not possible to give a coherent picture of what happens in terms of the classical mechanics. It is probably justifiable to say that the electric field does not make the individual electron move backward, but changes the relative probabilities of finding the electron moving in opposite directions; but since the whole effect is within the length of the wave packet, no detailed picture can be given. For many purposes it is justifiable to regard the electrons at the top of a band in the one-dimensional model of Fig. 73(*b*) as having a negative mass, or as behaving like particles with a positive charge. In the three-dimensional model, for electrons in states at the bottom of a zone, the effect of an electric field is to increase the value of k in the direction of the field, and the group velocity, v, is accelerated in the direction of F. As long

as the energy E can be expressed in the form of $Ak_x^2 + Bk_y^2 + Ck_z^2$ (*i.e.*, as long as the surfaces of constant energy are ellipsoids), equation V (11) is valid for the acceleration. As the surfaces of the zone are approached, the surfaces of constant energy become distorted, so that equation V (11) no longer holds, and in general a field F changes the group velocity, v, in directions other than that of F itself, so that force and acceleration are not in the same direction as regards the acceleration of the wave packet. For states near the top of a zone, the component of the velocity, v, perpendicular to the surface of the zone, decreases as the wave number k approaches the zone surface. The Brillouin-zone model of electrons in a periodic field has thus the characteristic that when there are comparatively few electrons in a zone, the group velocities, v, associated with the electron states behave very much like those of the free-electron model. On the other hand, if there is a completely filled or nearly filled zone, the electron states at the top of the zone are associated with the group velocities, v, which, under



[*Courtesy Clarendon Press.*

FIG. 85.

the influence of applied electric or magnetic fields, may vary as though the electron had a negative mass or a positive charge. It is in this way that the theory is able to account for the fact that in univalent metals the Hall coefficient * is negative, in agreement with the calculations of the simple electron theory, whereas in crystals with nearly full zones the Hall coefficient may be positive.

The preceding remarks refer to the motion of electrons in a strictly periodic field, and the Bragg reflections referred to above are the result of the periodicity of the field, and the effects described take

* The passage of a current down a rectangular conductor in the presence of a transverse magnetic field causes a difference in potential to be generated between the sides of the conducting plate. This is known as the Hall effect, and the Hall coefficient, r, is defined by the relation :

$$r = Ed/IH,$$

where E is the transverse potential difference, d the thickness of the plate parallel to the magnetic field of strength H, I the total current. By convention, the coefficient is positive if the electric potential is raised on that side of the plate on which the Amperean current generating the magnetic field has the same direction as the current I (Fig. 85).

place at the absolute zero. At this temperature, with small applied fields, crystals with perfectly regular structures will be insulators if they correspond with completely filled Brillouin zones of the type shown in Fig. 76(*b*), or perfect conductors if they possess incompletely filled zones. It can be shown that the atomic vibrations corresponding with the zero-point energy * do not produce an electric resistance, but as the temperature is raised, the ordinary thermal oscillations interfere with the perfect periodicity of the lattice, and a resistance is created. The theory is not able to explain the phenomenon of supraconductivity, which is found for some metals whose resistances remain zero for a few degrees above the absolute zero and then rise sharply to a finite value at a critical temperature. Supraconductivity is also destroyed by the application of a magnetic field above a certain critical intensity which varies with the temperature, but these and other allied phenomena † have so far defied explanation. As the temperature is raised, the Fermi surface marking out the limit of the occupied states in k-space becomes more diffuse, and qualitatively the picture of electrical resistance is very like that previously described for the simple free-electron theory. It is again only electrons near the surface of the Fermi surface of occupied states which can undergo collisions to affect the velocity distribution, and so create a resistance. It can be shown that, at temperatures which are not too low, the probability of an electron being scattered is proportional to the square of the displacement of an atom, and since the mean square of the displacement is proportional to the absolute temperature, the resistance should be proportional to the absolute temperature, in agreement with the observed facts; at low temperatures, however, the position becomes more complicated. The complete theory involves the interactions between the electrons and the lattice vibrations, and lies beyond the scope of the present book.

In univalent elements such as the alkalis and copper, silver, and gold, the first Brillouin zone is only half occupied, and interaction between an electron and a thermal vibration only transfers the electron concerned to a new state within the same zone. When, however, there are overlapping zones, and the boundary of the occupied states lies in the region of the overlap, these interactions may transfer the electron from a state in one zone to that in another. That is to say, an interaction with a lattice vibration may permit an electron to undergo a transition to a state which it would not reach under the influence of

* The zero-point energy is that due to atomic vibrations which persist at the absolute zero of temperature (see p. 262).

† See D. Schoenberg, "Superconductivity." Cambridge: 1938 (University Press).

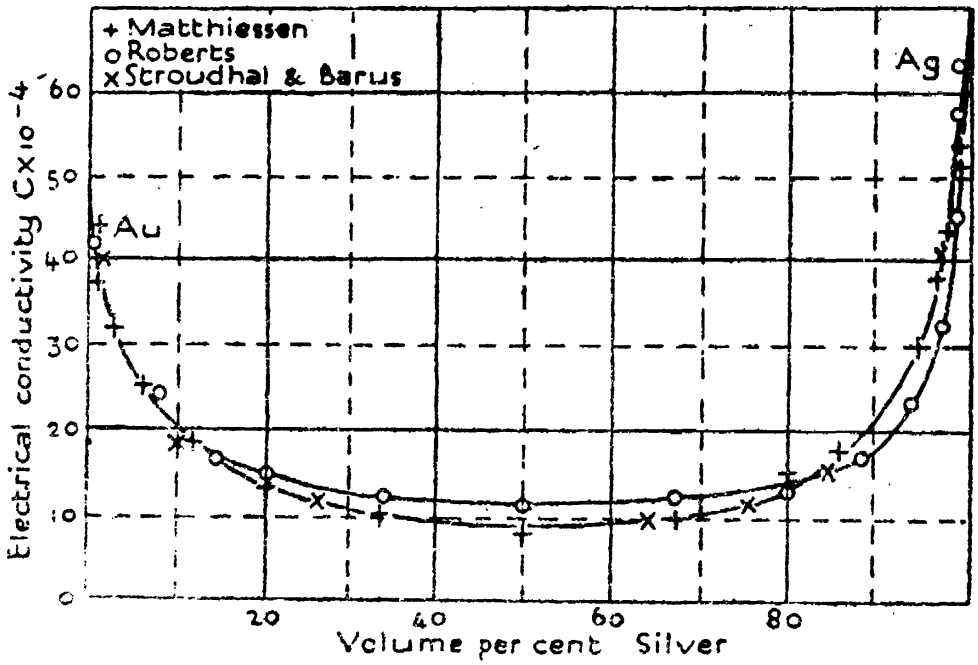
an electric field alone. The process is naturally very complicated, but, among other things, the probability of the transition is proportional to the density of states in the final state. It follows, therefore, that an abnormally great resistance is to be expected if the final state lies on a high part of an $N(E)$ curve. As we shall see later (p. 261), in the transition elements the electrons are in states derived from the s and d states of the free atoms, and the density of states in the d-band is always much the greater. In these elements the electric current is carried mainly by the s electrons, which behave more or less like those of the free-electron model, but the resistance is much greater than that of a normal metal because the interactions with the lattice vibrations may cause transitions from states in the s-band to those in the d-band, as well as the normal $s \longrightarrow s$ transitions. Further, for transition elements at very low temperatures, the effect of interactions between electrons, which is negligible for normal metals, becomes more important on account of the possibility of $s \longrightarrow d$ transitions, and at the temperature of liquid helium this kind of collision, which produces a resistance proportional to T^2, may be the predominant factor in determining the resistance of metals such as platinum and palladium.

When a solid solution is formed, the introduction of the solute atom upsets the perfect periodicity of the lattice, and this produces an increase in the electrical resistance. This increase in resistance in general remains as a residual resistance at the absolute zero * in contrast to the ordinary resistance due to the thermal vibrations, which vanishes at the absolute zero. In the alloys of silver with gold, the two atoms are of nearly the same size (p. 229) and of the same valency, and are therefore able to form a continuous series of solid solutions, since the crystal structures of the two elements are the same. Fig. 86 shows the specific conductivity of these alloys as a function of the composition, and the sharp fall in conductivity on the formation of the solid solution is clearly indicated. If a solid solution extends over a limited range of composition only, the conductivity/composition curve will resemble a portion of the curve in Fig. 86. Speaking generally, the decrease in conductivity for a given atomic percentage of solute is greater the greater is the difference between (*a*) the valencies, (*b*) the atomic diameters, and (*c*) the positions in the Periodic Table, of the solvent and solute.

When a random solid solution undergoes atomic rearrangement to form a superlattice (p. 110), the increased order of the structure is accompanied by a decrease in the electric resistance, and, generally

* With supraconducting metals a slight range of supraconducting solid solution may be formed in some cases.

speaking, any tendency to form an ordered structure favours a higher conductivity. This applies to intermediate phases in alloy systems as well as to primary solid solutions. Thus, in the system gold–zinc there is an intermediate phase with a body-centred cubic structure based on the composition AuZn, but with a considerable range of composition. Here the equiatomic alloy AuZn has the highest electrical conductivity, and corresponds with a completely ordered structure in which the gold atoms occupy the corners and the zinc atoms the centres of the body-centred cell (cæsium chloride type, see Fig. 47). Other alloys within this phase field have ordered structures in which like atoms tend to avoid being nearest neighbours, but when the



[*Courtesy Clarendon Press.*

Fig. 86.—The Electrical Conductivity of Gold–Silver Alloys.

numbers of the two different kinds of atoms are equal, the order is more perfect, and the conductivity greater. This relation between order and conductivity is the direct result of the wave-like characteristics of electrons.

The zone theory has thus enabled a considerable insight to be gained as to the processes involved in insulators and in normal metallic conductors. It remains to consider the class of substance known as semi-conductors, which are in general characterized by the fact that their electrical conductivity is increased by rise of temperature and by the presence of impurities, in contrast to the behaviour of normal metals. We may consider first a substance with the zone-characteristics shown in Fig. 87, where a fully occupied zone is separated from the

next zone by a very small gap. This substance would be an insulator at the absolute zero, but at high temperatures electrons would be thermally excited from the first to the second zone, and then, when in states at the bottom of the second zone, they would act as free electrons, and so give rise to a conductivity which would increase with the temperature, since the higher the temperature, the greater the number of electrons which would be excited into the second zone. It is important to note that it is the thermal excitation, and not the effect of the external electric field, which excites the electrons from one zone to another. In this type of semi-conductor, the electrons which are excited to the bottom of the upper zone behave like free electrons, and the Hall coefficient has the normal sign. Pure graphite is a semi-conductor of this type, but there are very few substances which are really semi-conductors in the pure state, and most semi-conductors owe their properties to the presence of impurities.

The second class of semi-conductor is due to the effect of impurities, and the condition of affairs is represented schematically in Fig. 88.

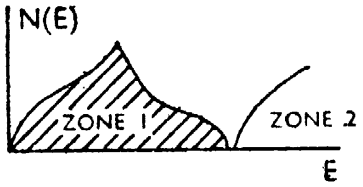


FIG. 87.

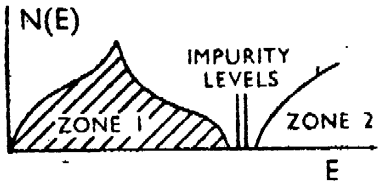


FIG. 88.

Here, a completely filled zone * (marked zone 1) and an empty zone (marked zone 2) are separated by a comparatively narrow energy gap. The effect of introducing impurity atoms is, in general, to create new energy levels, and it may happen that these lie within the energy gap, as shown in Fig. 88. At the absolute zero, the structure will be an insulator, but as the temperature is raised, one or both of two processes may occur.

(1) Electrons may be excited thermally from the impurity levels into the empty zone 2. These electrons will then enter states at the bottom of zone 2, where they will act as free electrons, so that a limited conductivity will be shown, and the Hall coefficient will have the normal sign.

(2) Electrons may be excited thermally from the top of zone 1 into the impurity levels. This will leave some of the states at the top of zone 1 unoccupied, so that the application of an electric field can cause a slight shift in the velocity distribution in zone 1, and so create a conductivity. As we have seen before, the effective

* The completely filled outermost zone need not, of course, be the first zone.

mass of electrons in states at the top of a zone is usually negative, and the mean velocities, v, associated with these states are affected by an electric field as though the electrons had a positive charge. In this case, therefore, the Hall coefficient has the opposite sign.

It will be appreciated that according to the nature of the zone structure and the numbers of electrons present, the above effects may give rise to semi-conductors in which the resistance increases with rise of temperature, as in a normal metal, or decreases with rise of temperature, the difference depending on the extent to which rise of temperature excites electrons into the conducting zone. Small amounts of impurity may produce marked differences because if the valency of the impurity atom is different from that of the solvent, the number of conducting electrons may be affected. These effects are thus complicated and depend greatly on the purity of the metal.

SUGGESTION FOR FURTHER READING.

Wilson, A. H. "Semi-Conductors and Metals. An Introduction to the Electron Theory of Metals." Cambridge: 1939 (University Press).

Chapter XXV.—More Complete Zone Theories.

In Chapters XXIII and XXIV we have described the characteristics of the simple zone theories in which the electrons are treated as moving in a regular periodic field. It is clear that this can only be an approximation to the real state of affairs, and that when an electron is near to an atom, the wave function and general characteristics of the electron will be related to the general structure of the atom concerned. The more complete zone theories try to take this into account, and the general picture presented is one in which an electron, when relatively near to an atom, is treated as though it were moving in the field of a free ion of the same structure as that existing in the metal. As emphasized on p. 57, the division of the outer electrons among the different sub-groups is not necessarily the same in a solid metal as in the free atoms of the same element, and this fact may have to be taken into account. In the case of the crystal of an alkali metal, for example, a valency electron when near to an atom is assumed to move in the field of a normal univalent positive ion, and hence in a manner analogous to that of a valency electron of a free atom. On the other hand, in the case of nickel, allowance would have to be made for the fact that the outer electrons of the free atom have the grouping $(3d)^8(4s)^2$, whereas in the solid metal (see p. 260) there are on the average only 0·4 electrons per atom in $(4s)$ states.

In Chapter XIII we have explained how, when atoms are brought together to form the crystal of a metal, the general characteristic is for each electron state of the free atom to broaden out into a band. We have explained further how in the case of crystalline sodium the bands derived from the $3s$ and $3p$-states have broadened out so much that they overlap, and the methods of soft X-ray spectroscopy show that s-states predominate at the bottom and p-states at the top of the first Brillouin zone. The next stage in the theory is clearly to see how the general conclusion of the simple zone theory will be affected if the assumption of a simple periodic field is replaced by a more detailed model in which the electrons acquire the characteristics of s-states, p-states, &c., of different atoms. For this purpose it is necessary to know the fields produced by the remaining electrons which build up the ion or core of the atom concerned. These fields are calculated by the method of the self-consistent field (see p. 67), and as this method is often only approximate, the results cannot be expected to be exact. The details of these calculations lie quite outside the

present book, although the general method due to Wigner and Seitz is described in Chapter XXVII. In general, these approximate methods are all attempts to describe the behaviour of electrons in terms of wave functions which, near to the nuclei, resemble those of free atoms in the appropriate electronic state, and which join up satisfactorily so as to produce acceptable solutions in the regions between the nuclei. Under these conditions, it may be said that an electron spends a certain time near to a given nucleus, and for this period it behaves very much as though it were in a free atom. It then spends a further period in travelling to an adjacent nucleus, and during this passage the electron may, in some metals (*e.g.*, the alkalis), behave very much as in the simple *free-electron theory*, whilst in other metals the behaviour may be entirely different.

Provided we are dealing with electrons in *s*-states, the general characteristics of the simple zone theory are retained, except that the normal electronic mass m is replaced by the effective electronic mass m^*, which may be different from m. The relation between E and k is of the same general form as that of Fig. 73(*b*), and at the bottom of the first zone the relation between E and k is of the form :

$$E = \frac{h^2k^2}{8m^*\pi^2},$$

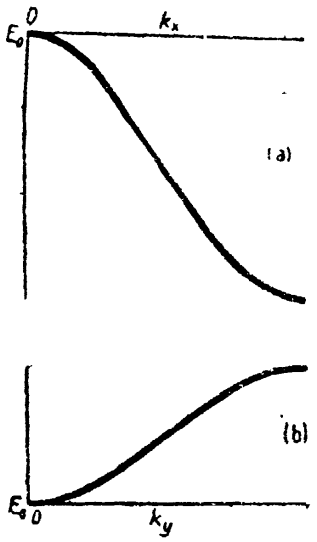
where m^* may be greater or smaller than the normal electronic mass m. It is interesting to note that for sodium, m and m^* are very nearly equal, which is another reason why sodium is such a good approximation to an ideal metal.

In the same way the $N(E)$ curves of the more complete theories of electrons in *s*-states are of the same general form as those of the simple zone theory. At the bottom of the first zone $N(E) \propto E^{\frac{1}{2}}$, and the constant of proportionality is equal to $2\pi\left(\frac{2m^*}{h^2}\right)^{3/2}$, where m^* replaces the m of the simple theory. Similarly, at the bottom of higher zones, $N(E) \propto \sqrt{E - E_0}$, where E_0 is the energy of the lowest state in the zone concerned, and the constant of proportionality involves the effective electron mass, which may be different for the different zones in a given metal. At the top of each zone $E \propto \sqrt{E_\omega - E}$, where E_ω is the energy of the highest state in the zone concerned. As in the simple zone theories, the velocity, v, associated with a state is proportional to dE/dk, and this proportionality always holds, irrespective of whether the electron is in an *s*, *p*, or *d*-state. If the surfaces of constant energy in k-space are spherical, an external field accelerates the electron in the direction of the field, *i.e.*, force and acceleration of

the wave packet are in the same direction, and the acceleration is proportional to d^2E/dk^2. If we write the effective electronic mass, m^*, as :

$$m^* = \frac{h^2}{4\pi^2} \Big/ \frac{d^2E}{dk^2},$$

the effective electronic mass may be very different from that of the simple zone theories. If the effective electronic mass is very small, the acceleration produced by a given field will be correspondingly large, so that a few electrons with a small effective electronic mass may produce a higher conductivity than a large number of electrons with a normal electronic mass.

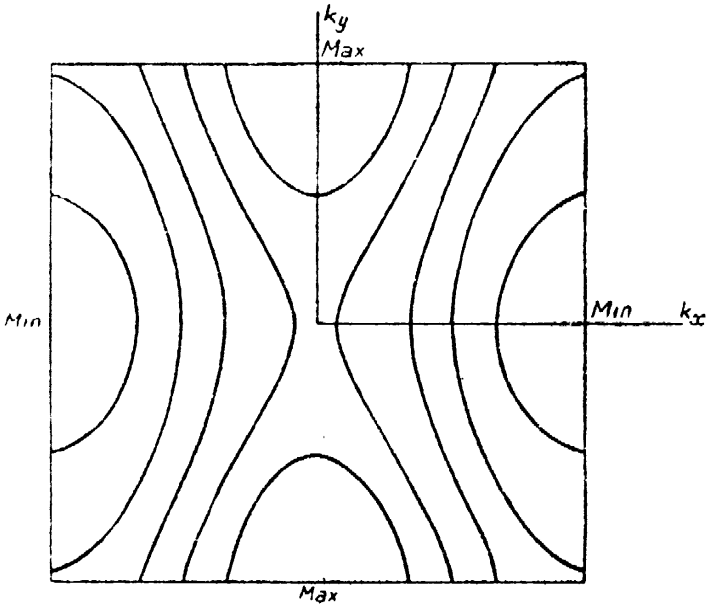


[*Courtesy Clarendon Press.*

FIG. 89.—This figure shows the E/k relations for a p-band in which the electron cloud is stretched out along the x-axis. E increases with k in the y and z directions, but decreases with k in the x-direction, *i.e.*, in the direction in which the electron cloud is most dense. This is in contrast to the E/k relations for s-states, where E increases with k in all directions.

It will be seen that for electrons in s-states the conclusions of the more complete zone theories are essentially the same as those of the simple theory, except that the effective electron mass m^* replaces the normal electronic mass. This is the result of the spherical symmetry of the s-states, and for the p-states the position is very different. In Chapter XII we have seen that when an atom is placed under sufficient restraint for the x, y, and z-axes to have a physical meaning, the electron clouds of the three p-states are mutually perpendicular, and of the form shown in Fig. 22. We may now imagine that we are dealing with an electron in a p-state in which the nodal plane is perpendicular to the x-axis, and the electron cloud stretches out along the x-axis. We may consider the relation between the energy E and the wave number k_y, where k_y is in the direction parallel to the y-axis. This relation is of the form shown in Fig. 89(b), and is of the same general form as the curve for s-states. The energy increases with the wave number, and the E/k curve is of such a form that d^2E/dk^2 is positive at the bottom of the band and negative at the top. Similar considerations apply to the relation between k_z and E, where k_z is along the z-axis. Fig. 89(a) shows the relation between E and k_x, where k_x refers to states along the x-axis. This is of quite a different form, and the energy diminishes with increasing wave number, and dE/dk is negative, whilst d^2E/dk^2 is negative at the top of a band and

positive at the bottom. It follows, therefore, that electrons with small wave numbers along the k_x-axis, *i.e.*, in the direction of the densest part of the electron cloud, will, under the influence of an electric field, behave as though they had a positive charge, although those with wave numbers along the k_y or k_z-axes will behave normally. This behaviour is the result of the symmetry of the p-functions, and the form of the energy contours in k-space is naturally greatly influenced by the fact that E increases with increasing k in the k_y and k_z directions, but decreases with k in the k_x direction. It will be appreciated that this means that for states in the k_x direction, the states of lowest



[*Courtesy Clarendon Press.*

FIG. 90.—This figure shows the contours of constant energy in the xy plane of k-space for a p-band in which the electron cloud is stretched out along the x-axis in real space, the crystal structure being simple cubic. In the direction of k_x, E decreases with k, as shown in Fig. 89, whilst in the k_y direction E increases with k. The states of highest and lowest energy are therefore in the regions marked max. and min., respectively. This is in contrast to the condition of affairs in an s-band, where the states of lowest energy are at the centre of the zone.

energy have the highest wave number. In the simple zone theory, and in the case of s-states, E increases with k for all directions, so that, although the field of the crystal lattice distorts the energy contours from a spherical form, we can say that for any direction in k-space E increases with k, continuously within a zone and discontinuously at a zone boundary. With p-states, however, E may either increase or decrease with increasing k, according to the direction relative to the crystal axes. If, for example, we consider a simple cubic structure and construct surfaces of constant energy in three-dimensional k-space, then a section parallel to the k_xk_y plane will show lines of constant energy, and these have the form illustrated in Fig. 90, which is due to Mott and Jones. For a given distance from the origin of k-space,

these contours show a minimum energy in the k_x direction, *i.e.*, in the direction in which in real space the electron cloud is most dense.

The characteristics of the p-states referred to above imply that with overlapping Brillouin zones, the directions in which the overlaps first occur may be quite different from those of the simple zone theory. In the simple theory, where E increases with k in all directions, there is a general tendency for the overlap to occur first across the surface of the zone which is nearest to the origin, but this is clearly not necessarily the case when p-states are concerned. Thus in Fig. 90 the electrons of lowest energy would occupy states in the regions which have been marked " min.," and which start from one of the zone boundaries.

The general conclusion of the Bloch theory, that $(E - E_0) \propto k^2$, and $N(E) \propto (E - E_0)^{\frac{1}{2}}$, where E_0 is the energy at the bottom of a zone, always applies to the electron states as a whole, whether these are assumed to be entirely of an s, p, or d-type, or are a mixture of the different types as in actual metals. We have explained above that when s and p-states are considered there is a general tendency for s-states to predominate at the bottom and p-states at the top of the first zone, although each type extends over the whole width of the zone. In such a case the theory indicates that in an actual crystal the relative numbers of s and p-states are distributed so that, at the bottom of a zone :

$$N(E)_s \propto (E - E_0)^{\frac{1}{2}}$$

and

$$N(E)_p \propto (E - E_0)^{\frac{3}{2}}$$

where $N(E)_s$ and $N(E)_p$ refer to the number of s and p-states in the mixture of states of which the band consists. The total $N(E)$ for the states as a whole at the bottom of the zone varies as $(E - E_0)^{\frac{1}{2}}$ in the usual way. Similarly, for a band consisting of s, p, and d-states, these are distributed so that :

$$N(E)_{s+d} \propto (E - E_0)^{\frac{1}{2}}$$

and

$$N(E)_p \propto (E - E_0)^{\frac{3}{2}}.$$

It is this kind of relation which is responsible for the different shapes of the $N(E)$ curves referred to in Part III in connection with the soft X-ray emission spectra, and in all cases the total $N(E)$ varies as $(E - E_0)^{\frac{1}{2}}$ at the bottom of a band. The reader will find that some descriptions are very confusing on this subject, and easily give rise to the wrong conclusion that $N(E)_p \propto (E - E_0)^{\frac{3}{2}}$ for a hypothetical band consisting entirely of p-states. The correct position is that the variation as $(E - E_0)^{\frac{3}{2}}$ applies to the actual number of p-states in a band consisting of a mixture of s, p, and d-states. A hypothetical band consisting of p-states only would give $N(E) \propto (E - E_0)^{\frac{1}{2}}$ at the bottom of the band.

PART VI.—ELECTRONS, ATOMS, METALS, AND ALLOYS.

CHAPTER XXVI.—THE ALKALI METALS.

1. *General.*

THE alkali metals lithium, sodium, potassium, rubidium, and cæsium all crystallize in the body-centred cubic structure, the unit cell of which is shown in Fig. 36 (p. 101). These elements are the nearest approach to the "ideal metals" of the electron theories, and they are characterized by the fact that the electron clouds of their ions are small compared with the distances between the atoms in the crystals of the metals. In Fig. 91 we show the $\rho(r)$ curves for the outer parts of the *free ions* of the alkali metals as a function of the distance from the

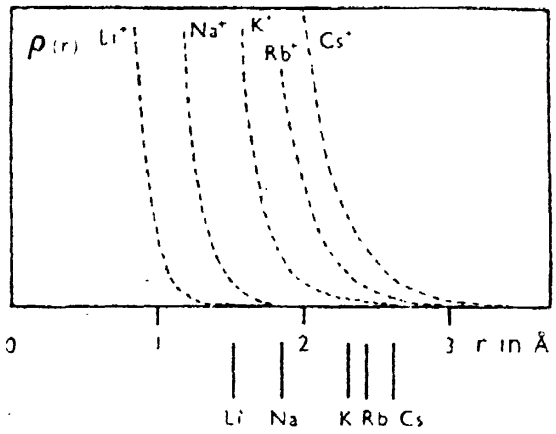
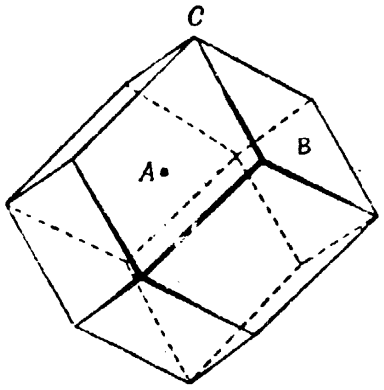


FIG. 91.—The $\rho(r)$ Curves for the Outer Part of the Ions of the five alkali metals as a function of the distance (r) from the nucleus. The five vertical lines are at distances equal to one-half the closest distance of approach of the atoms in the crystals of the pure metals. The vertical scale is arbitrary, but is the same for all five curves, and is the same as that of Fig. 98.

nucleus, and we indicate also one-half the nearest distance of approach of the *atoms in the crystals of the metallic elements*. It will be seen that in lithium and sodium the electron cloud of the ion has almost vanished at the point midway between the atoms in the metal, whilst in potassium, rubidium, and cæsium the density of the cloud is very small. As the centre of the ion is approached the electron cloud density becomes very large. Strictly speaking, the electron cloud patterns of the ions are slightly different in the metals and the free atoms, but the difference is small, and Fig. 91 is a good approximation for the electron clouds of the ions in the solid metals. When it is remembered

that the volume varies as the cube of the dimensions, it will be seen that the volumes in which the electron cloud densities of the ions are appreciable are only small fractions of the total volumes of the metallic crystals. Metals of this kind may conveniently be called "open metals." Metals for which the electron clouds of the ions overlap considerably may be called "full metals." The alkali metals form the most open group of metals, and they may be regarded as consisting of relatively small ions maintained in regular array by the valency electrons. The overlap of the ions is thus very small, and the resulting forces have a negligible effect in determining the binding energies or the lattice spacings. The forces resulting from the slight overlap of the ions vary rapidly with the distance, and these forces play a slight part in determining the compressibilities, and a considerable part in determining the elastic constants of the alkali metals. The properties of the alkali metals are thus determined mainly by the valency electrons, and it is for this reason that the alkali metals are of such interest in developing theories of metals, even though they are too reactive to be of any practical value as the main constituents of alloys.



[*Courtesy Clarendon Press.*

FIG. 92.—The First Brillouin Zone of the Body-Centred-Cubic Lattice. The zone is a regular dodecahedron; *A* is the centre of a face, and is one of the points on the surface which is nearest to the origin; this is therefore one of the points where a spherical Fermi surface first touches the zone boundary. It should be noted that the corners of the zone are not all equivalent; the corner *C* lies at a greater distance from the centre of the zone than the corner B.

The body-centred cubic structure gives rise to a first Brillouin zone of the form shown in Fig. 92. This zone contains two electron states per atom, and is bounded by dodecahedral planes, in agreement with the fact that the first strong diffraction line from a body-centred cubic structure is that from the (110) dodecahedral planes. Since the alkali metals contain only one valency electron per atom, the zone is only half filled, and it is the natural assumption of all the theoretical work that the Fermi surface of occupied states is approximately spherical, and that it does not touch the surface of the zone. This assumption has been called in question by the work of Skinner on the soft X-ray spectra of solid sodium. The L_3 emission band of sodium observed by Skinner is shown in Fig. 29 (p. 92), and it will be seen that there are signs of a slight kink at the high-energy end. Skinner takes this to indicate that although there is only one electron per atom, the Fermi surface has penetrated the first Brillouin zone, and that

an overlap into the second zone has started. This, of course, would be in direct contradiction to the simplifications, which involve the assumption that the Fermi surface is almost spherical, in which case the surface of the first zone is reached only when there are about 1·48 electrons per atom (see p. 240). There are difficulties in accepting Skinner's interpretation, since with one electron per atom, an overlap into the second zone would imply a Fermi surface very different from a sphere, and this would suggest a considerable energy gap at the zone boundary which is not indicated by the emission curves. For the moment this discrepancy is unexplained.

2. *Alloys of the Alkali Metals.*

In Chapter XV we have seen how the tendency for two metals to form primary solid solutions is controlled first by the "size-factor." Fig. 93 shows the interatomic distances in the crystals of the elements; the well-marked periodicity is apparent, and in each period the alkali metals have the largest atomic diameter. The alkali metals are all univalent, and all crystallize in the same structure (body-centred cubic), and consequently the conditions for comparison are as favourable as possible. In Table IV are shown the lattice spacings and

TABLE IV.—*Lattice Spacings and Interatomic Distances of Alkali Metals.*

Metal.	Lattice Spacing, kX.	Interatomic Distance, kX.	Increase in Atomic Diameter, %.
Li	3·5023 at 20° C.	3·0331	} 22
Na	4·2820 at 25° C.	3·708	} 25
K	5·333 ,,	4·618	} 5·5
Rb	5·62 at −173° C.	4·87	} 7·6
Cs	6·05 ,,	5·24	

interatomic distances in the crystals of the alkali metals, and also the percentage increase in atomic diameter (defined by the closest distance of approach of the atoms) on passing from one element to the next. Fig. 94 shows diagrammatically the equilibrium diagrams of the alloys formed by different pairs of the alkali metals, so far as they are known. It will be seen that no wide solid solutions are formed in the systems where the atomic diameters differ by more than the critical value (14–15%) which was referred to in Chapter XV. On the other hand, continuous solid solutions are formed in the systems K–Rb, K–Cs, and Rb–Cs, where the size-factors are favourable. This tendency for elements of the same sub-group, and of the transitional elements, to form solid solutions with one another was pointed out by

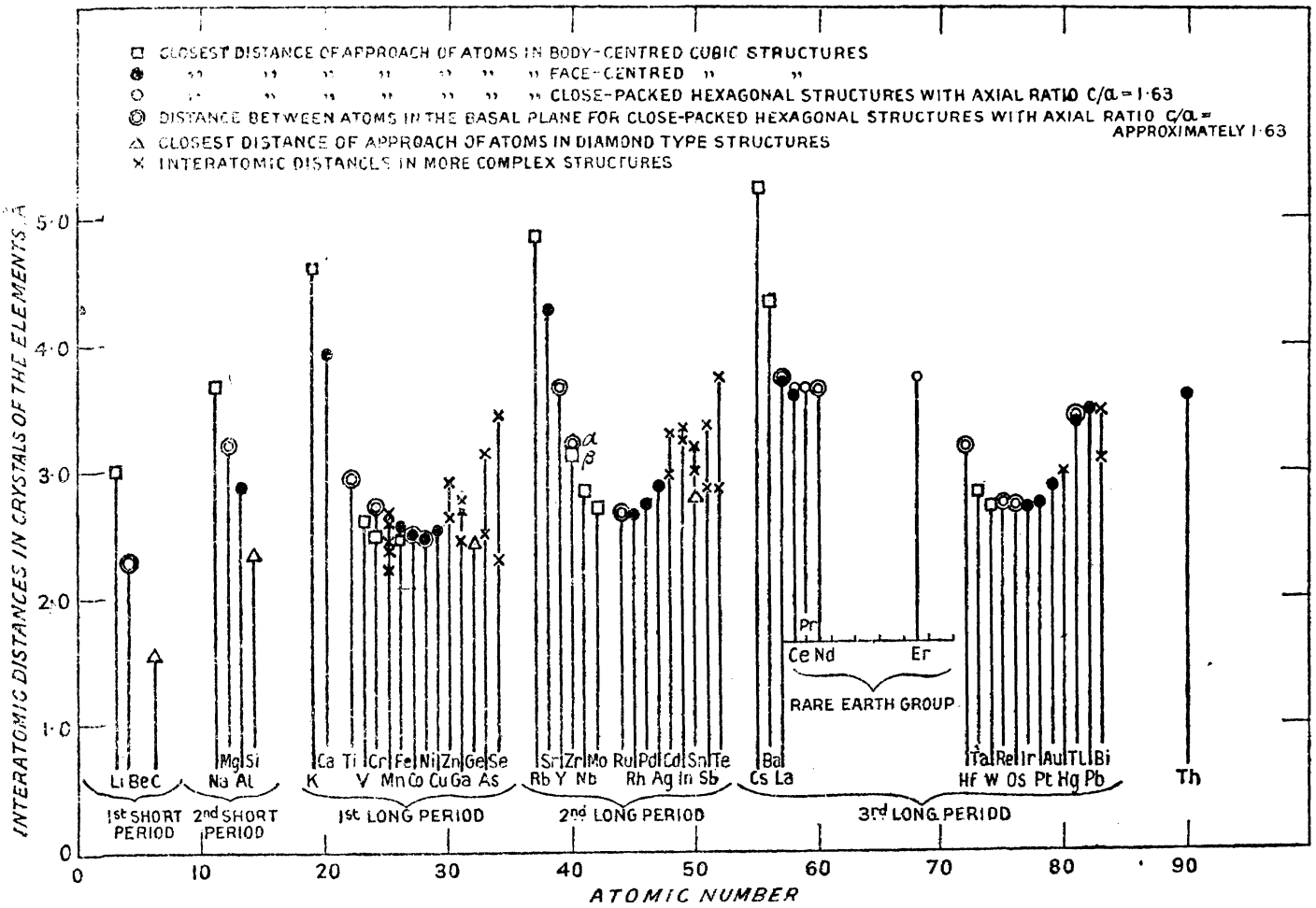


FIG. 93.—Interatomic Distances in the Crystals of the Elements.

van Liempt as long ago as 1926, and later work has confirmed that, apart from the size-factor effect, different kinds of atoms fit together more easily on a common lattice if their valencies are the same, *i.e.*, if they contribute the same number of valency electrons per atom.

We have already seen in Chapter XV that when we deal with pairs of metals which differ markedly in the electrochemical series, there is a tendency to form stable intermediate phases at the expense of the primary solid solutions. In general, the alkali metals are so electro-

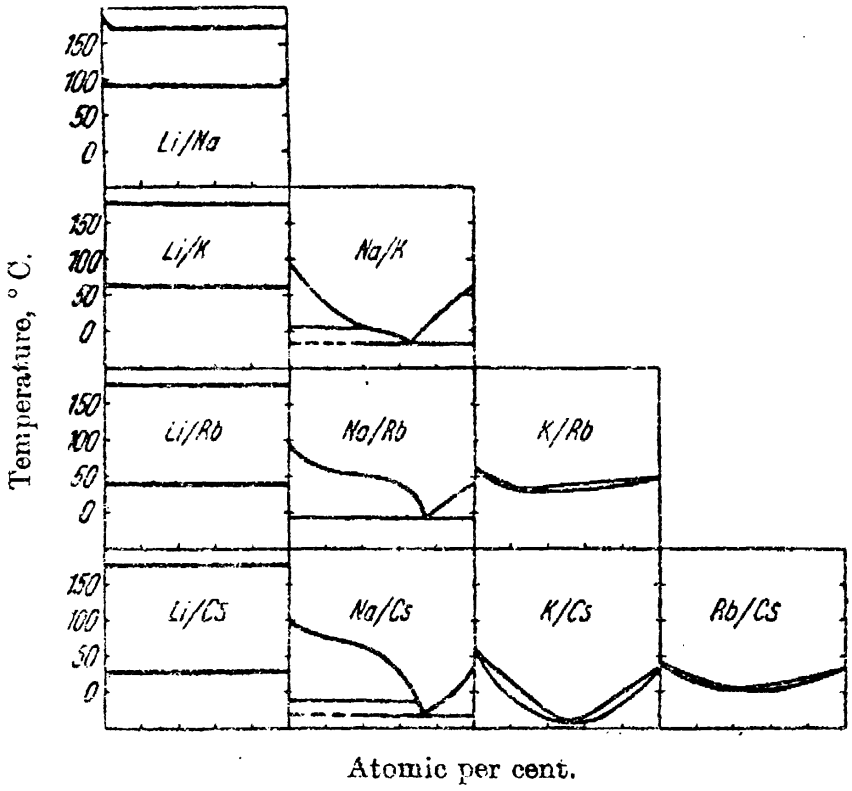


FIG. 94.—Equilibrium Diagrams of the Binary Alloys of the Alkali Metals with One Another. Immiscible liquids are formed in the systems Li–Na, Li–K, Li–Rb, and Li–Cs. Continuous solid solutions are formed in the systems K–Rb, K–Cs, and Rb–Cs (from Böhm and Klemm, *Z. anorg. Chem.*, 1939, 243, 69).

positive compared with other metals that solid solutions in the alkali metals are comparatively rare, even where the size-factors are favourable.

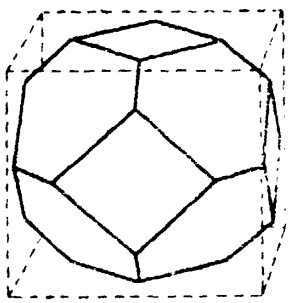
3. *The Method of Wigner and Seitz: The Ideal and Real Metal.*

We have seen that the more complete zone theories result in the description of the electron by means of wave functions which, near to each atomic nucleus resemble those of a free atom, and which then join up satisfactorily in the regions between the atoms. One of the most successful ways of dealing with this problem is due to Wigner and Seitz, and was developed first for the alkali metals. In the body-

centred cubic structure, if a is the side of the unit cube, each atom has eight neighbours at a distance $a\sqrt{3}/2$ and six at a distance a. In this case if we draw planes to bisect the lines joining an atom to its closest and next closest neighbours, these planes form a truncated octahedron such as that shown in Fig. 95. If we imagine each atom to be surrounded by an octahedron of this kind, the octahedra will join up and completely fill the crystal. With other crystal structures a similar treatment can be applied, and the polyhedra obtained are called "atomic polyhedra," "s-polyhedra," or "atomic cells." * The wave function for the lowest state is periodic with the period of the lattice, and is symmetrical about any nucleus, and consequently the boundary condition assumed is that at the boundary of any atomic polyhedron :

$$\frac{\partial\psi}{\partial n} = 0$$

where the differentiation is normal to the boundary. This boundary condition allows the wave functions to join up smoothly in the space between two atoms.



[*Courtesy Clarendon Press.*

FIG. 95.—Atomic Cell of Body-Centred Cubic Lattice.

It will be seen that the atomic polyhedron of Fig. 95 is not very different from a sphere, and the next assumption made is that the polyhedron may be replaced by a sphere of equal volume, so that if Ω is the atomic volume, the radius r_0 of the atomic sphere is defined by :

$$\tfrac{4}{3}\pi r_0^3 = \Omega \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{VI (1)}$$

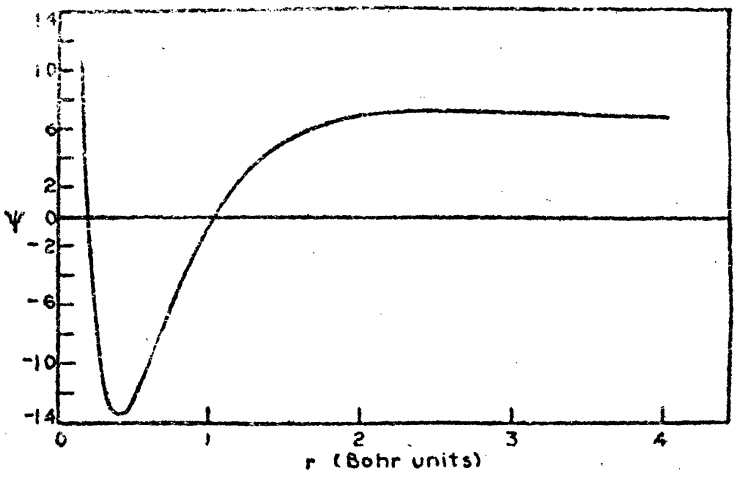
It is important to note that this radius is a hypothetical concept, defined by the above relation, and that it is not equal to one-half the closest distance of approach of the atoms in the crystal. The polyhedron having been replaced by the sphere, the boundary condition assumed is that $\frac{\partial\psi}{\partial n}$ vanishes everywhere on the surface of the sphere.

The variation of the potential inside the atomic sphere is taken from calculations of the self-consistent-field type (see p. 67), and the calculation of the wave function of the valency electrons consists of the solution of the Schrödinger equation for an electron moving in this potential field, subject to the condition that $\frac{\partial\psi}{\partial n}$ vanishes on the

* The Wigner–Seitz atomic polyhedra must, of course, in no way be confused with Brillouin zones. The latter are in k-space, and show the surfaces in k-space at which the energy changes discontinuously. The atomic polyhedra are in real space, and show how real space may be divided up so that each atom is surrounded by a similar polyhedron, the different polyhedra fitting together to occupy the whole space of the crystal.

surface of the sphere, and to the normalizing condition that there is one electron per atom. The general problem is very complicated, and the following additional assumptions are therefore made in the case of the alkali metals.

(1) It is assumed that at any instant there is only one electron in each atomic sphere. For univalent metals this is a reasonable assumption, but it has, of course, to be abandoned when metals of higher valency are dealt with. The electrons tend to avoid each other, owing to their mutual electrostatic repulsion on the one hand, and also on account of the Pauli Exclusion Principle, as a



[*Courtesy Physical Review.*

FIG. 96.—The Wave Function of the Lowest State of the Valency Electrons in a Crystal of Pure Sodium. The electron cloud density of the valency electron at a distance r from the nucleus is proportional to the value of ψ^2 at the distance concerned. The distance between two adjacent atoms in the crystal is 3·71 A. = 7·01 Bohr units.

result of which electrons of the same spin can very seldom be in the same atomic cell.

(2) In the simple Wigner–Seitz theory it is assumed that the electron clouds of the ions do not overlap, and that the mutual interaction of the electron clouds can be ignored.

It is then possible to calculate the wave function for the valency electron in the lowest electron state of the crystal, and Fig. 96 shows the value of ψ as a function of the distance along the line joining two atoms which are closest neighbours in the crystal of sodium. It will be seen that the ψ curve has two nodal points on each side of a given nucleus, in agreement with the general principle that the electron cloud of a 3*s* state has $3 - 1 = 2$ nodes. It will also be noted that the curve is almost horizontal for a relatively large part of

the distance between two adjacent atoms, and it is this fact which makes the free-electron model a justifiable approximation for the alkali metals. When it is remembered that the volume is proportional to the cube of the distance, it will be appreciated that for the greater part of the volume of the crystal of sodium, the valency electron may be treated as though it were an electron in the free-electron model.

The energy associated with the ψ curve of Fig. 96 can then be used to calculate the binding energy of the crystal, which is defined as the work required to dissociate the crystal into free neutral atoms, and is thus the same as the heat of sublimation. It is very necessary to make quite clear the meaning of the symbols used in this connection, since the descriptions in some papers and books are unfortunately confusing. We may denote by E_I the ionization potential of a free atom of sodium, so that E_I is the work required to separate a neutral atom into a free positive ion and a free electron. We may now imagine that we have an assembly of atoms at very large distances from one another. Then, since the atoms are widely separated, their interaction may be ignored, and the work required to remove separately one electron and one positive ion will be equal to E_I. If the positive ion and the electron recombine to form a neutral atom, the work evolved will again be E_I, and the binding energy will then be zero. We may now suppose that the atoms assemble together to form a crystal of sodium. The energy of the valency electrons is then spread over a range or band, and the work required to remove the electron in the lowest state, *together with one positive ion*,* may be denoted $-E_0$, and is a function of the distance between the atoms.

The convention of a negative sign is used so that the values of E_0 will indicate the energy of the crystal in the sense that the firmer the binding the lower the energy and the more stable the structure.†

* It is here that some of the descriptions are so very confusing, since they readily give the impression that E_0 is the work required to remove *an electron* in the lowest state from the crystal. The heat of sublimation, however, refers to the removal of a complete atom (electron plus ion), and the term E_0 must therefore be defined so as to include the work required to remove the positive ion as well as the electron.

It should be pointed out that when defined with reference to the neutral atom, the binding energy is not a measure of the strength of the cohesion in the solid. Thus, if in the case of sodium we had a hypothetical structure in which all the eleven electrons of each atom were separated from the nuclei and took part in the binding process, the cohesive forces would be enormous, and an immense quantity of energy would be required to separate the crystal into free ions and electrons. But when these electrons and ions recombined to form neutral atoms, most of this energy would be given out, and the binding energy as defined above would be correspondingly diminished. The binding energy is, of course, a quite definite physical constant, but for some purposes the melting point is a better measure of the strength of the cohesive forces in a solid.

† Thus, if the work required to remove an electron and an ion from one structure

If the electron and the positive ion then recombine to form a neutral atom, the energy evolved will be E_I, and consequently $(-E_0 - E_I)$ represents the net work required to remove from the crystal one positive ion and one electron in the lowest state, and then to allow them to recombine to form a neutral atom. If all the electrons in the crystal were in the lowest state, then $-(E_0 + E_I)$ would give the binding energy or heat of sublimation per atom. Actually, however, the electronic energies extend over the whole range of the Fermi distribution, and an electron in a high-energy state naturally requires less work for its removal than does an electron in the lowest energy state. If the symbol E_F is used to denote the mean Fermi energy of the electrons, with the lowest electronic state taken as zero, then the binding energy of the crystal as a whole will clearly be $-(E_0 + E_F + E_I)$ as compared * with the value $-(E_0 + E_I)$ which would hold if all the electrons were in the lowest state. Since $-(E_0 + E_F + E_I)$ is the work required to evaporate the electrons and ions from the crystal and convert them into neutral atoms, the energy of the crystal relative to the free atom is $+(E_0 + E_F + E_I)$. Large values of E_F or E_I thus tend to make the energy of the crystal greater than that of free atoms, and hence to make the crystal relatively less stable. For any given metal, E_I is a constant of the free atom, whilst both E_0 and E_F are functions of the distance between the atoms. As explained above, E_F is the mean Fermi energy, and in the free-electron model E_F is simply the kinetic energy of the translatory motion of the electrons, while in the zone theories E_F is that part of the energy associated with the motion of the electrons in the periodic field of the lattice; as explained before (p. 189) this cannot always be interpreted as the energy of long-range translatory motion. As defined above, E_0 is the work required to break up or dissociate into free electrons and positive ions a hypothetical crystal in which all the electrons are the lowest energy state. In a simple model which ignored the atomic characteristics, E_0 would involve only the *potential energy of the hypothetical crystal* in which all the electrons occupied the lowest energy states.† In the more complete theories, E_0 involves both potential and kinetic energy, because, as can be seen from Fig. 96, even in an alkali metal the wave function near to an atom is no longer constant, and this leads to a kinetic energy.

were 10 cal., and from another structure 1000 cal., we should have $-E_1 = 10$ and $-E_2 = 1000$, and hence $E_1 = -10$ and $E_2 = -1000$, and the energy E_2 would be lower than the energy E_1.

* It will be appreciated that with the above convention of signs, E_0 is negative and E_F and E_I are positive. When the atoms are infinitely far apart E_F is zero and E_0 and E_I are numerically equal but of opposite sign.

† It is essential to note that the term E_0 refers to the energy of the crystal, and is not the work required to remove one electron from the lowest state.

For the alkali metals it is possible to calculate both E_0 and E_F for different values of r_0, and, as shown in Fig. 97, the curve for $(E_0 + E_F)$ passes through a minimum which is not very far removed from the minimum on the curve for E_0 alone. The equilibrium condition will clearly be that corresponding to the minimum on the curve for

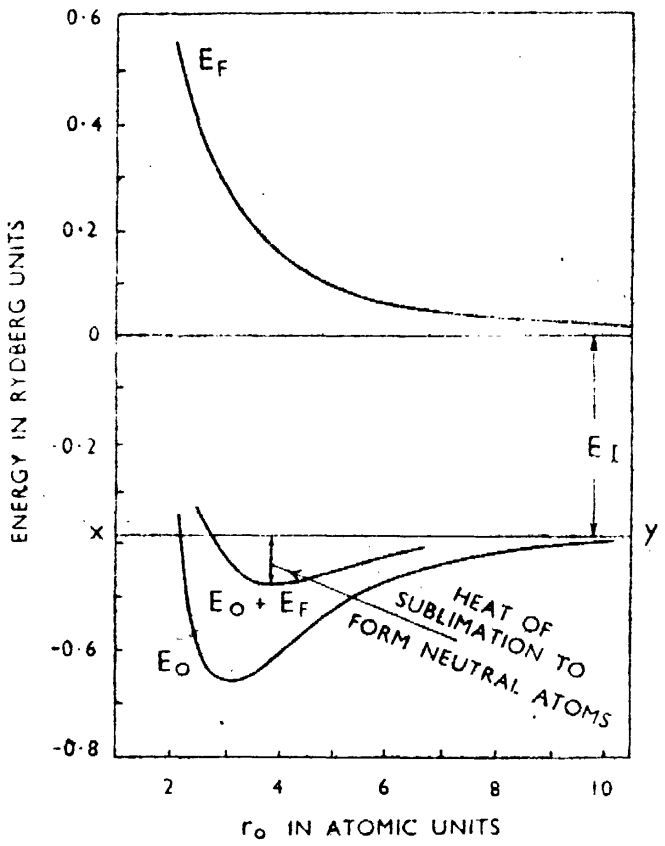


FIG. 97.—The lowest curve shows the variation of E_0 with r_0 (for the definition of these quantities see p. 220). If all the electrons were in the lowest state, the position of the minimum on this curve would indicate the equilibrium value of r_0 at the absolute zero of temperature. Actually only two electrons can occupy the lowest state, and it is necessary to add the mean Fermi energy E_F, which is itself a function of r_0. The uppermost curve shows the variation of E_F with r_0, and the curve marked $E_0 + E_F$ is obtained by the summation of the curves for E_0 and E_F. The minimum on the curve marked $E_0 + E_F$ indicates the equilibrium value of r_0, and the curvature in the region of the minimum permits a calculation of the compressibility. The line xy lies below the zero of energy at a distance equal to E_I, the ionization potential of a free atom of sodium. The distance between xy and the minimum of the curve $E_0 + E_F$ indicates the heat of sublimation.

$(E_0 + E_F)$, and in this way it is possible to calculate the value of r_0, and hence also the atomic volume and lattice spacing of the metal at the absolute zero of temperature. The binding energy is then equal to $-(E_0 + E_F + E_I)$, and since the curves of Fig. 97 express the energy as a function of the atomic volume,* it is possible to calculate

* It will be remembered that r_0 is defined by the relation $\frac{4}{3}\pi r_0^3 = \Omega$, where Ω is the atomic volume.

the compressibility K, by means of the relation :

$$\frac{1}{K} = -v\left(\frac{dp}{dv}\right) = v\left(\frac{d^2E}{dv^2}\right) \quad . \quad . \quad . \quad . \quad \text{VI (2)}$$

where E is the total energy.

In general it may be said that for the alkali metals the agreement between theory and experiment is satisfactory. The various methods used differ in the degree to which simplifying assumptions are introduced. The simplest treatment of all is due to Fröhlich and may be called that of *the ideal metal.* In this the essential assumptions are that :

(1) The electron clouds of the ions are small compared with the distances between the atoms, so that their overlapping can be ignored.

(2) The effective electronic mass is unity and the Fermi distribution is spherical, so that the mean Fermi energy E_F can be calculated from the simple free-electron theory. In Part IV we have seen that E_F is proportional to $\left(\frac{N}{V}\right)^{2/3}$, where N is the number of electrons in volume V, and hence E_F is proportional to $\frac{1}{r_0^2}$; the constant of proportionality is approximately 2·2 if energy is measured in Rydberg units, and the unit of length is the radius of the first Bohr orbit (see p. 72).

(3) All correlation effects arising from the fact that two electrons cannot be at the same place at once can be ignored.

Subject to these simplifying assumptions, Fröhlich shows that the energy of the crystal which we have previously written $(E_0 + E_F + E_I)$ can be expressed in the form :

$$-\frac{3}{2}\frac{e^2}{r_0} + \frac{2{\cdot}2}{r_0^2} + \frac{1}{2}\frac{e^2R^2}{r_0^3} + E_I \quad . \quad . \quad . \quad . \quad \text{VI (3)}$$

Here the first term represents the potential energy, and is inversely proportional to r_0. The second term is the Fermi energy E_F referred to above, and is inversely proportional to r_0^2. The third term represents the kinetic energy of the lowest electron state (see p. 221), and the term assumes its comparatively simple form—inversely proportional to r_0^3—because the parts of the wave function of Fig. 96 which give rise to the kinetic energy are near the nucleus and are not affected by small variations in r_0. The constant R differs from one alkali metal to another, and can be calculated from the ionization energy,

or from the experimental value of r_0. In this way it is possible to calculate the binding energy and the compressibility of the alkali metals at the absolute zero, and, except for lithium, reasonable agreement is obtained with the values found by experiment at other temperatures. The failure of the theory in the case of lithium is thought to be due to the effective electronic mass m^* being different from m.

The equations for the ideal metal of Fröhlich have been generalized by Bardeen, who writes the energy of the crystal of an alkali in the form:

$$-\frac{A}{r_0}+\frac{B}{r_0^2}+\frac{C}{r_0^3}+E_F \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{VI (4)}$$

and then determines A, B, and C from the experimental values of the lattice constant, the heat of sublimation, and the compressibility at zero pressure. The equation thus obtained is then used to calculate the variation of the compressibility with the pressure, and reasonable agreement with the experimental data is obtained.† This method is justifiable in the case of lithium, because although the effective electron mass m^* differs from the normal mass m, the energy and the wave number are still related by an equation of the type:

$$E=\frac{h^2k^2}{8m^*\pi^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{VI (5)}$$

The above theories of the alkali metals involve the assumption that at any instant each atomic cell contains only one electron, and that the correlation effects can be ignored, and also the effects of the electron clouds of the ions on one another. Attempts have been made to extend the theory, and the following points have been established for the alkali metals.

The assumption that the atomic polyhedron may be replaced by an atomic sphere produces a negligible error. The mutual interaction of the electron clouds of the ions is very small in the alkali metals, and has a negligible effect on the binding energy, but the forces involved vary rapidly with the distances. Fuchs extended the theory to include the calculation of the elastic constants by a method in which the energy changes were calculated for deformations which produced a change of shape without a change of volume, and it was found that the interaction of the electron clouds of the ions produced a considerable effect in determining the elastic constants, and a slight effect on the compressibility.

The more important corrections to the simple theory of the alkali metals concern the assumption that there is at a given instant only one electron in an atomic polyhedron, and that correlation effects concerning the mutual positions of the electrons can be ignored. For purposes of calculation these effects are usually classed under three headings. In the first place the electrostatic interaction is calculated between a given electron and other electrons in the same atomic polyhedron, assuming no correlation between the positions of the electrons. This gives rise to a repulsion which decreases the binding force and increases the energy of the crystal by an amount equal to $\frac{0{\cdot}6e^2}{r_0}$. Secondly, there is the exchange energy resulting from the fact that electrons with the same spin tend to avoid each other on account of the Pauli Principle. This results in an attractive force which diminishes the energy by an amount equal to $\frac{0{\cdot}458e^2}{r_0}$. Thirdly, electrons of opposite spin tend to avoid one another, and this produces an attractive force which lowers the energy of the crystal by an amount equal to $\frac{be^2}{r_0}$, where b is of the order of 0·1 for the alkali metals. It will be seen, therefore, that the correlation effects as a whole produce energies of attraction and repulsion which nearly cancel each

† The experimental data have, of course, to be adjusted to refer to the absolute zero.

other, so that the conclusions of the simple Wigner–Seitz theory remain essentially correct.

REFERENCES AND SUGGESTIONS FOR FURTHER READING.

Electronic Structure of Sodium.
E. Wigner and F. Seitz, *Phys. Rev.*, 1933, [ii], **43**, 804; 1934, [ii], **46**, 509.
E. Wigner, *ibid.*, 1934, [ii], **46**, 1002.
J. Bardeen, *J. Chem. Physics*, 1938, **6**, 367.

Electronic Structure of Lithium.
J. Bardeen, *op. cit.*

Theory of Compressibility and Elastic Constants.
K. Fuchs, *Proc. Roy. Soc.*, 1936, [A], **153**, 622; **157**, 444. (The second paper corrects mistakes in the first.)

General Theory.
H. Fröhlich, *Proc. Roy. Soc.*, 1937, [A], **158**, 97.

Much of this work is summarized in "The Modern Theory of Solids," by F. Seitz. New York: **1940** (McGraw-Hill Book Co., Inc.); and in "The Theory of the Properties of Metals and Alloys," by N. F. Mott and H. Jones. Oxford: **1936** (Clarendon Press).

Chapter XXVII.—Copper, Silver, and Gold.

1. *General.*

Copper, silver, and gold in Group IB are univalent metals whose atoms contain one valency electron outside a closed group of 18. They all crystallize in the face-centred-cubic structure (Fig. 36, p. 101). Fig. 98 shows the electron cloud density $\rho(r)$ curve for the free *ion*, Cu^+, and the lower vertical line shows one-half the closest distances of approach of the atoms in the *crystal of pure copper*. When this figure is compared with the corresponding diagram (Fig. 91) for the alkali metals, it will be seen that in the crystal of copper there is a much greater overlap of the electron clouds of the ions. The fact that the electron clouds of the ions overlap so much means, of course, that the curve of Fig. 98 is not an accurate representation of the actual state of affairs in the metal, although it does show clearly that the ionic overlap is considerable. The repulsive forces resulting from this ionic overlap vary rapidly with the interatomic distance, and it is for this reason that the compressibility of copper is so much smaller than those of the alkali metals. There is a general tendency for the compressibility of a metal to increase with the atomic volume, but as can be seen from Fig. 99, the compressibilities of the alkali metals are so much greater than that of copper that the effect cannot be due solely to the greater atomic volumes of the alkali metals. Similar considerations apply to silver and gold, and the pronounced ionic overlap in these metals means that, as pointed out by Mott and Jones, the crystals of copper, silver, and gold may be regarded as built up of hard spheres (ions)

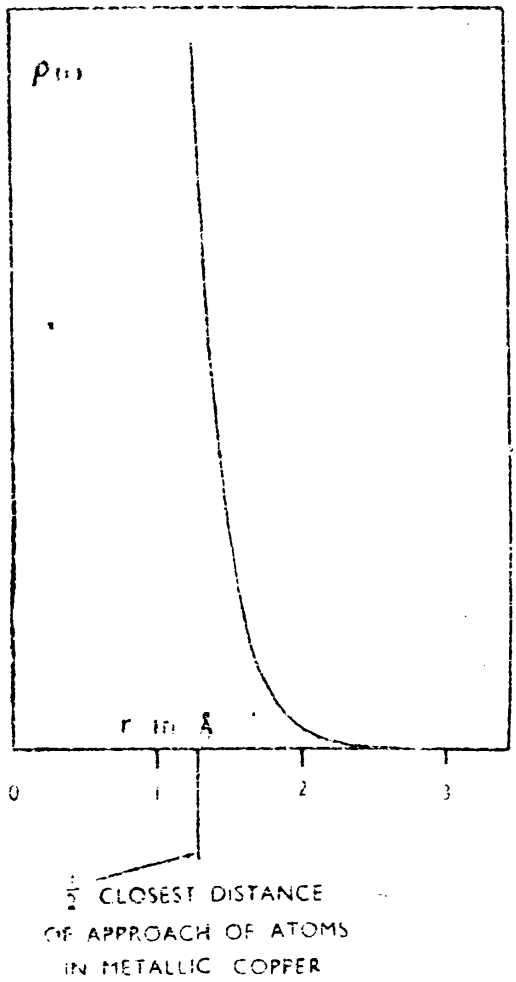


Fig. 98.—The $\rho(r)$ Curve for the outermost part of the Cu^+ Ion. The vertical scale is arbitrary, but is the same as that of Fig. 91.

held in contact by the valency electrons, in contrast to the alkali metals, where the ionic overlap is so small that it accounts for only a small fraction of the repulsive force. It has been shown by Fuchs that if the compressibility of copper is calculated by the methods of Wigner and Seitz without allowing for the effect of the ionic overlap, the calculated value is from 4 to 8 times that observed experimentally;

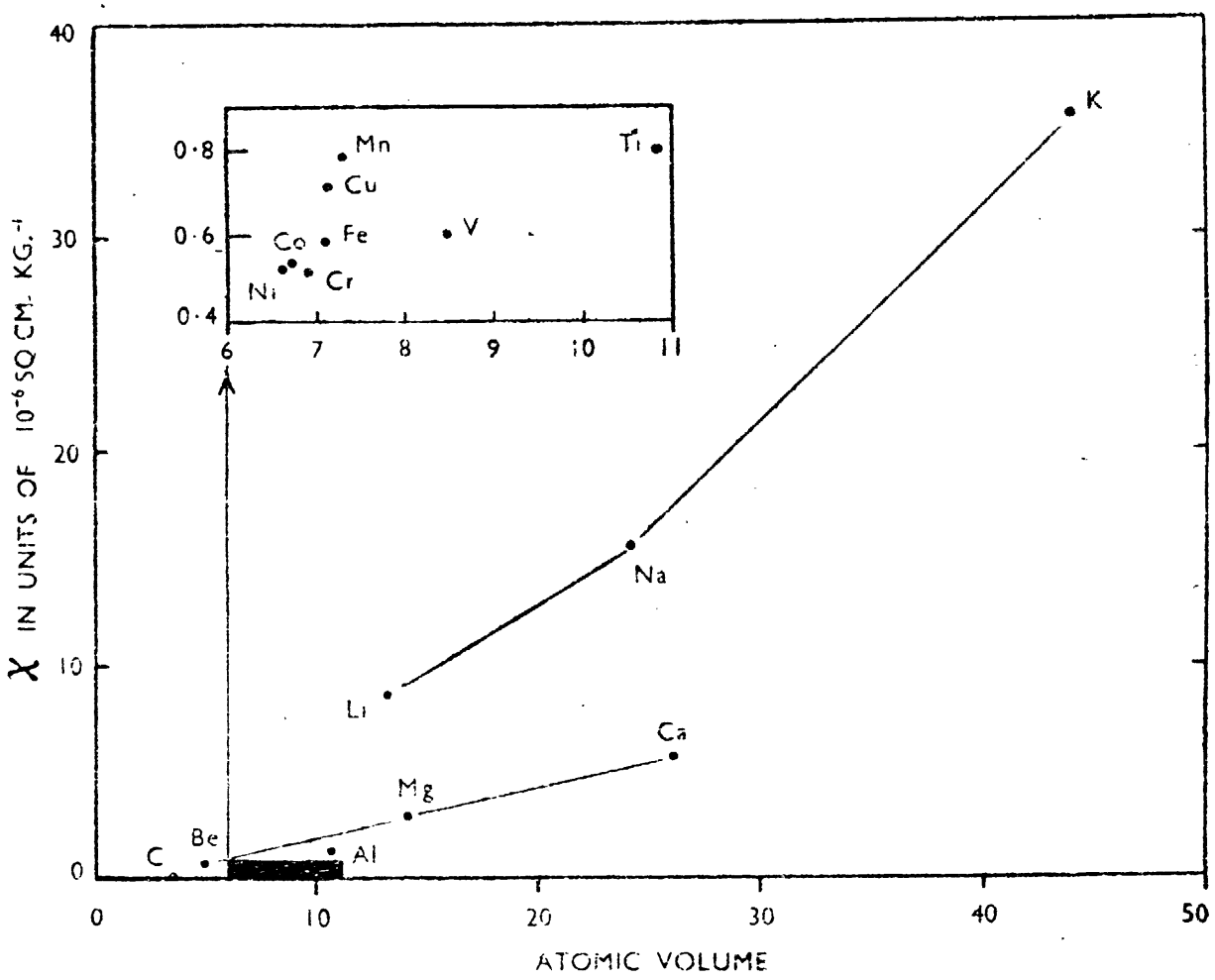


FIG. 99.—Compressibilities of the Metals of Lower Atomic Number plotted against their atomic volumes. The points for Li, Na, and K, and for Be, Mg, and Ca show the general tendency for the compressibilities to increase with atomic volume. The compressibilities of the elements Ti–Cu are very much smaller, and this is due to the overlap of the electron clouds of the ions.

whilst if the ionic overlap is allowed for, a good agreement is obtained between the calculated and observed values.* The resistance of copper to compression is thus largely the result of the ionic overlap, and the same factor plays a predominant effect in determining the elastic constants. The work of Fuchs has also shown that for copper, when the energy of the ionic overlap is taken into account, the face-

* Calculations have not been made for silver and gold.

centred cubic structure is more stable than a body-centred cube, and we can thus understand why copper crystallizes in the face-centred structure. In the case of the alkali metals, however, there is little difference between the energies calculated for the two structures, and the fact that all these elements crystallize in the body-centred cubic structure has not yet been explained theoretically.

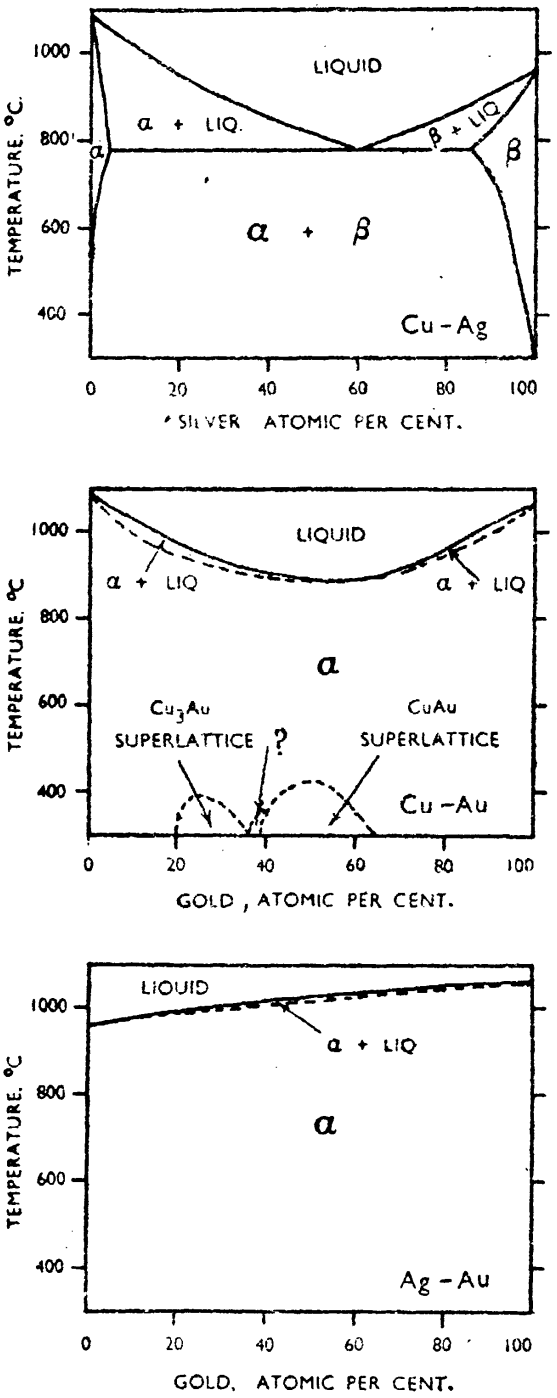


FIG. 100.—The Equilibrium Diagrams of the Systems Cu–Ag, Cu–Au, and Ag–Au.

The first Brillouin zone of the face-centred cubic structure has been illustrated in Fig. 75 (p. 185), and as there is only one valency electron per atom in copper, silver, and gold, the zone is only half-filled, and the position of affairs is assumed to be that of Fig. 75(*a*) in which the Fermi surface of occupied states has not touched the surface of the zone. The surfaces of the zone nearest to the occupied states are the [111] planes, and those next nearest are the [200] planes; this corresponds with the fact that the first two strong X-ray reflections from face-centred cubic crystals have the indices [111] and [200].

The lattice spacings and interatomic distances in copper, silver, and gold are shown in Table V, and Fig. 100 shows the equilibrium diagrams of the systems copper–silver, copper–gold, and silver–gold. It will be seen that a continuous solid solution is formed in the system silver–gold, where the size-factors are very favourable. In the systems copper–gold and copper–silver the size-factors are almost identical, and are on the borderline of the favourable zone. Here it will be seen that the copper–silver alloys form a simple eutectiferous system, with com-

paratively restricted solid solutions. In the system copper–gold the size-factor is almost the same as in the system copper–silver, but as will be seen from Fig. 100, copper and gold are completely miscible in the solid state at high temperatures, although well-defined superlattices exist at low temperatures. The presence of these superlattices is undoubtedly due to the fact that the atomic diameters of gold and copper are on the borderline of the favourable zone, because this means that the formation of a solid solution is accompanied by a considerable strain which may to some extent be relieved by a regular

TABLE V.—*Lattice Spacings and Interatomic Distances of Copper, Silver, and Gold.*

Metal.	Lattice Spacings, kX.	Closest Interatomic Distance, kX.	Increase in Atomic Diameter, %.
Cu	3·6078 at 18° C.	2·5511	13
Ag	4·0779 at 25° C.	2·8835	<1
Au	4·0704 ,,	2·8782	

arrangement of the atoms. It is, however, clear from Fig. 100 that atoms of copper and gold tend to fit together more easily than atoms of copper and silver in spite of the size-factors being the same in the two systems. This is probably the result of the fact that the ion of gold is more easily polarizable than the ion of silver. This means that the electron cloud of the gold ion can be more easily distorted, and so can fit more readily into the copper lattice than the ion of silver. This serves to emphasize the limitations of attempts to represent the size of an atom by a single constant, and the polarization effects have been discussed in detail by Hume-Rothery and Raynor.*

2. *The α/β Brass Equilibrium.*

In the alloys of copper, silver, and gold with one another, the atoms are all univalent, and so the electron concentration is 1·0. As stated above, the calculations show that at this electron concentration the face-centred and body-centred cubic structures would be equally stable if the valency electrons alone were concerned, and that the face-centred cubic structure is preferred owing to the forces produced by the overlap of the electron clouds of the ions. When copper, silver, and gold are alloyed with B-sub-group elements of higher valency, the electron concentration is increased, and the study of this class of alloy has thrown much light on the principles underlying alloy

* *Phil. Mag.*, 1938, [vii], **26**, 129.

formation. In Chapter XV we have described the main characteristics of the equilibrium diagram of the system copper–zinc (Fig. 43, p. 109), and we have seen how with increasing zinc content, the α-solid solution in copper is succeeded by the β, γ, and close-packed hexagonal phases, and that structurally analogous phases are found in other alloy systems, the characteristic being that a phase of a given structure occurs at roughly the same electron concentration (p. 113). It is sometimes possible to interpret these effects in terms of the Brillouin zone theories, and to show that these theories explain the stability of the particular structure at the electron concentration concerned. In the simple theory of the subject it is assumed that in systems where the size-factor is favourable, the alloying of copper or silver with elements of higher valency is a process in which the addition of the solute element serves merely to increase the electron concentration. This work is due largely to H. Jones, and to understand it we may consider briefly how electron concentration affects the stability of a phase. We may suppose that Fig. 101 shows the $N(E)$ curve for the first Brillouin zone of a structure X, which is not overlapped by the curve for the second zone. The point A represents the stage at which the Fermi surface touches the surface of the zone. The fall in the $N(E)$ curve beyond A means that the number of energy states per unit energy range is decreasing rapidly, and hence the increase in energy for the addition of a given number of electrons increases rapidly beyond A. If, therefore, we compare the crystal structure X with another structure Y for which the $N(E)$ curve remains high beyond the point A, then as far as electron concentration is concerned, the structure X will become less stable than Y as the electron concentration increases * from A to B to C, since the most stable structure will be that which accommodates the electrons with the lowest energy. It will further be appreciated that the more nearly a Brillouin zone approximates to a sphere, the more nearly the curve ABC will be vertical.† The theory of Jones may then be summarized by saying that on increasing the electron concentration, there will be a general tendency for a phase to be stable

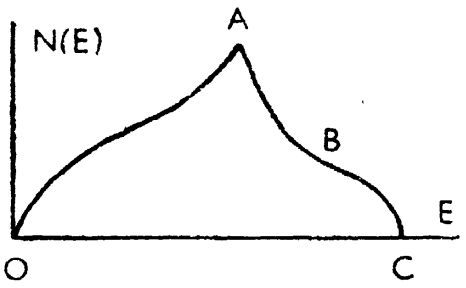


FIG. 101.

* In all this discussion we assume, of course, that the addition of electrons is accompanied by an addition of positive electricity to keep the structure electrically neutral. In practice the increase in electron concentration is brought about by alloying with an element of higher valency.

† If the Brillouin zone were spherical, and the Fermi surfaces of constant energy were also spherical, the line ABC would be vertical, since the energy at which the surface of the zone was reached would be the same in all directions.

at the electron concentration corresponding to the point A, but to become unstable in the region of the rapid fall $A \longrightarrow B$ in Fig. 101, because, on account of the large number of possible crystal structures, there will probably be some other structure for which the $N(E)$ curve remains high, and which can therefore accommodate the electrons with a lower energy.

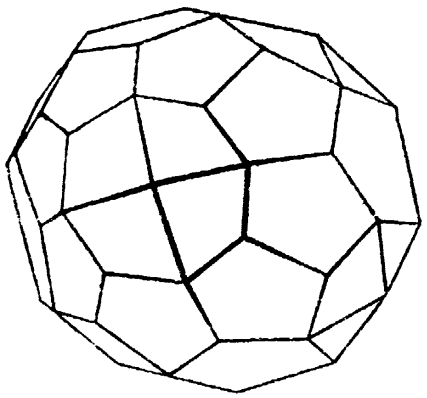
If, in Fig. 101, the first zone is overlapped by a second zone, the total $N(E)$ curve will begin to rise again at the stage where the overlap begins, and Jones has shown that the effect of an overlap is to produce an expansion of the crystal lattice in a direction parallel to the direction of the overlap in the Brillouin zone. In this way it has been possible to explain some of the lattice-spacing/composition relationships in the close-packed hexagonal phase in the system copper–zinc, and these effects are referred to later in connection with magnesium (p. 244) and aluminium (p. 253).

A simple calculation (see Appendix, p. 239) shows that in the face-centred cubic structure the point A in Fig. 101 occurs at an electron concentration of 1·36, and hence with atomic compositions of 36 and 18 at.-% of divalent and trivalent solutes, respectively. We shall therefore expect a tendency for the face-centred cubic structure to become unstable when the electron concentration exceeds this value, and it will be noted that in many alloys of copper and silver with elements of higher valency, the α-phase boundary occurs at about this electron concentration.

In the body-centred cubic structure the point A (Fig. 101) occurs at an electron concentration of 1·48, and hence at a higher electron concentration than the first peak in the $N(E)$ curve for the face-centred cubic structure. At an electron concentration of 1·48 (*i.e.*, 48 at.-% of a divalent solute, and 24 at.-% of a trivalent solute) we shall therefore expect the body-centred cubic structure to be more stable than the face-centred cube, since the $N(E)$ curve for the latter has fallen, whilst that for the former is at its peak. This is in agreement with the empirical discovery (p. 114) that body-centred cubic phases tend to occur at an electron concentration of 1·5. At higher electron concentrations we shall expect the body-centred cubic phase to become unstable. Actually when the size-factor is favourable, the composition of the β-phase at high temperatures usually extends to an electron concentration greater than 1·48, and the reason for this is possibly that the dodecahedral Brillouin zone for the body-centred cubic phase (Fig. 92, p. 214) is not a very good approximation to a sphere, so that the curve AB in Fig. 101 does not fall very steeply.

In the β-manganese structure, the first Brillouin zone has the shape

shown in Fig. 102, and approximates more nearly to a sphere. The number of electrons necessary to fill the zone completely is 1·62 per atom, and a sphere inscribed within the zone corresponds with 1·41 electrons per atom, so that the fall from *A* to *B* to *C* in Fig. 101 is much more rapid for the β-manganese structure than for the body-centred cube where the completely filled zone and the inscribed sphere correspond with 2·0 and 1·48 electrons per atom respectively. It is perhaps significant that in systems where the β-manganese structure exists, its boundaries do not greatly exceed the electron concentration 1·5. The theory of Jones has explained satisfactorily the existence of body-centred cubic and β-manganese structures at an electron concentration of 3/2, and of γ-brass and close-packed hexagonal structures at electron concentrations of 21/13 and 7/4, respectively, but it suggests that so far as electron concentration is concerned there is no reason to expect a simple whole-number ratio. The theory has not, however, succeeded in accounting for the existence of close-packed hexagonal structures at the electron concentration 3/2. The theory enables us to understand in a general way why a phase tends to become unstable at the electron concentration where the $N(E)$ curve falls steeply and far, but since the solubility limit represents equilibrium between two phases, the details of the process depend on the relative energy characteristics and $N(E)$ curves of the two phases concerned. If these are known, it is possible in principle to calculate the exact position of the phase boundary, as in the case of the α/β-brass equilibrium described below, but very few calculations of this kind have been made.



[*Courtesy Clarendon Press.*

FIG. 102.—Brillouin Zone for the β-Manganese Structure. The structure is cubic with 20 atoms in the unit cell. The Brillouin zone shown is bounded by (221) and (310) planes, and the complete zone corresponds to 1·62 electrons per atom. The inscribed sphere of the zone corresponds to 1·41 electrons per atom.

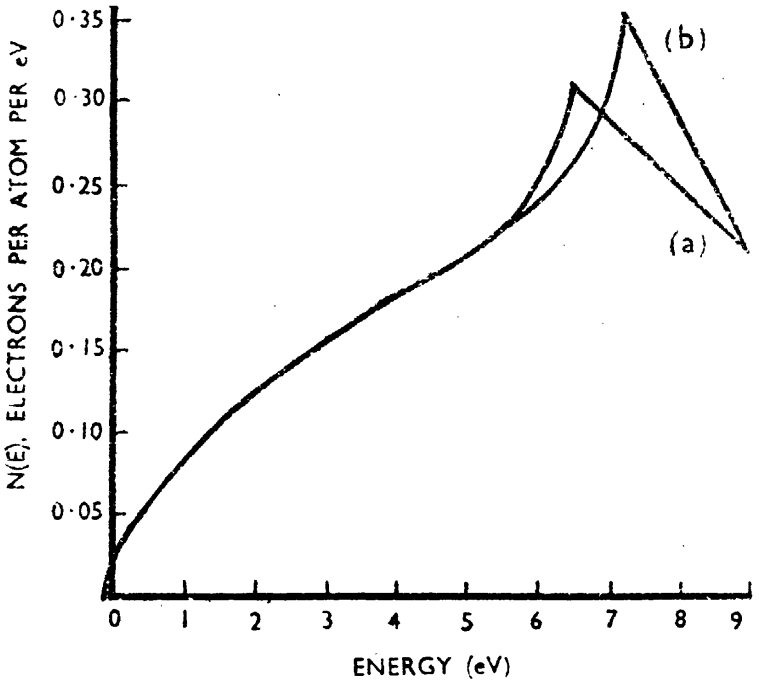
When we come to consider the position of a phase boundary of an electron compound on the side of low electron concentration, the situation is less definite, since even if the electron concentration is the predominant factor, it is only when the relative shapes of the $N(E)$ curves from *O* to *A* in Fig. 101 are known for two structures that we can begin to estimate the point at which the phase boundary is to be expected. There is, however, a number of cases in which electron compounds are found to exist over a range of compositions situated

almost entirely on the high electron-concentration side of the characteristic ratio. Thus, in the γ-brass structures the composition of the phase in a particular system often extends over a considerable range,* but lies almost entirely on the high electron concentration side of the ratio 21 electrons to 13 atoms which characterizes the structure. This phenomenon is probably due to the existence of something approaching co-valent linkages in these structures. For, as pointed out by J. D. Bernal in 1927, if there are homopolar bonds involving a definite number of electrons, it will be far more serious to have too few electrons than to have too many. We have already seen (p. 196) that the co-valency and Brillouin zone theories are to be looked upon as complementary rather than as antagonistic, and these co-valency effects may often be important. Thus the diamond type of structure, which from the one viewpoint is regarded as giving rise to a completely filled Brillouin zone, is also quite properly regarded as a structure where each atom exerts its normal co-valency of 4, and we should not expect this structure (*e.g.*, germanium or silicon) to dissolve an element of lower valency, because there would be insufficient electrons to form the co-valent bonds. We might, however, find a ternary solid solution with two elements, one of higher and one of lower valency, in proportion adjusted to maintain a ratio of 4 valency electrons per atom.

With normal metallic phases, the phase boundary in a binary equilibrium diagram represents equilibrium between two phases, and the form of the boundary naturally depends on the nature of the crystal structures concerned. Reference to Figs. 43 and 45 (pp. 109 and 115) will show that the $\alpha/(\alpha + \beta)$ and $(\alpha + \beta)/\beta$ phase boundaries have a characteristic form in which the solubility limit of zinc or gallium in the face-centred cubic or α-phase diminishes as the temperature rises. This kind of equilibrium has been investigated by H. Jones, who accepted the hypothesis of Hume-Rothery, Mabbott, and Channel-Evans that electron concentration was the predominant factor when the size-factors were favourable. The work of Jones may be understood by means of Fig. 103, which shows the $N(E)$ curves for face-centred and body-centred cubic structures, subject to the assumption that the energy discontinuities are the same at the faces of the first Brillouin zones. The peak on the curve for the body-centred cube (*b*) corresponds with the [110] direction in the crystal, and the peak on the curve for the face-centred cubic structure (*a*) refers to the [111] direction. These curves relate to the absolute zero of temperature, and they show that although at the lower energies the two $N(E)$ curves

* In the system copper–zinc (Fig. 43) the γ-phase region lies mainly, but not entirely, on the high electron-concentration side of the characteristic ratio.

are indistinguishable, there is an energy range where the curve for the body-centred cube rises markedly above that for the face-centred cube. Now the higher the $N(E)$ curve, the greater is the number of electrons which can be accommodated in states within the range of energy concerned, and hence the lower the energy necessary to accommodate a given number of electrons. It follows, therefore, that at the absolute zero of temperature, so far as the Fermi energy is concerned, there is a point at which the body-centred cubic structure becomes more stable than the face-centred cube, since the body-centred cubic structure is able to accommodate the number of electrons con-



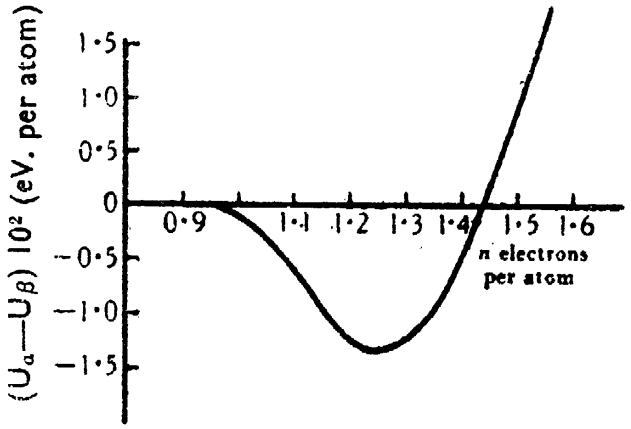
[*Courtesy Physical Society.*

FIG. 103.—Curves showing the number of states per unit energy range as a function of the energy (*a*) for the face-centred cubic, and (*b*) for the body-centred cubic structure.

cerned with a lower energy. The shapes of the curves in the neighbourhood of the peaks depend on the magnitude of the energy gap, ΔE, at the surface of the zones, and the optical properties of copper indicate that $\Delta E = 4{\cdot}1$ e.v. Using this value, it is possible to calculate the difference in energies of the face-centred cubic and body-centred cubic structures at the absolute zero, and the results are shown in Fig. 104, from which it will be seen that when the electron concentration exceeds 1·44, the body-centred cubic structure has the lower energy. It is also possible to calculate the energy of each structure as a function of the electron concentration, and it can be shown that for electron concentrations from 1·0 to about 1·4, the lowest energy

will be given by the face-centred cubic or α-phase alone. For electron concentrations between about 1·40 and 1·44 the lowest energy is given by a mixture of the α and β phases, whilst with electron concentrations above 1·44 the lowest energy is given by the body-centred cubic phase alone.

These calculations refer to the absolute zero of temperature, and the theory has not yet been able to explain the curious slope of the $\alpha/\alpha + \beta$ phase boundary in which the solubility of zinc in copper increases as the temperature falls (see Fig. 43, p. 109). The original paper * of H. Jones claimed to calculate the correct slope of the $\alpha/\alpha + \beta$ and $\alpha + \beta/\beta$ phase boundaries, but later work * by C. Zener



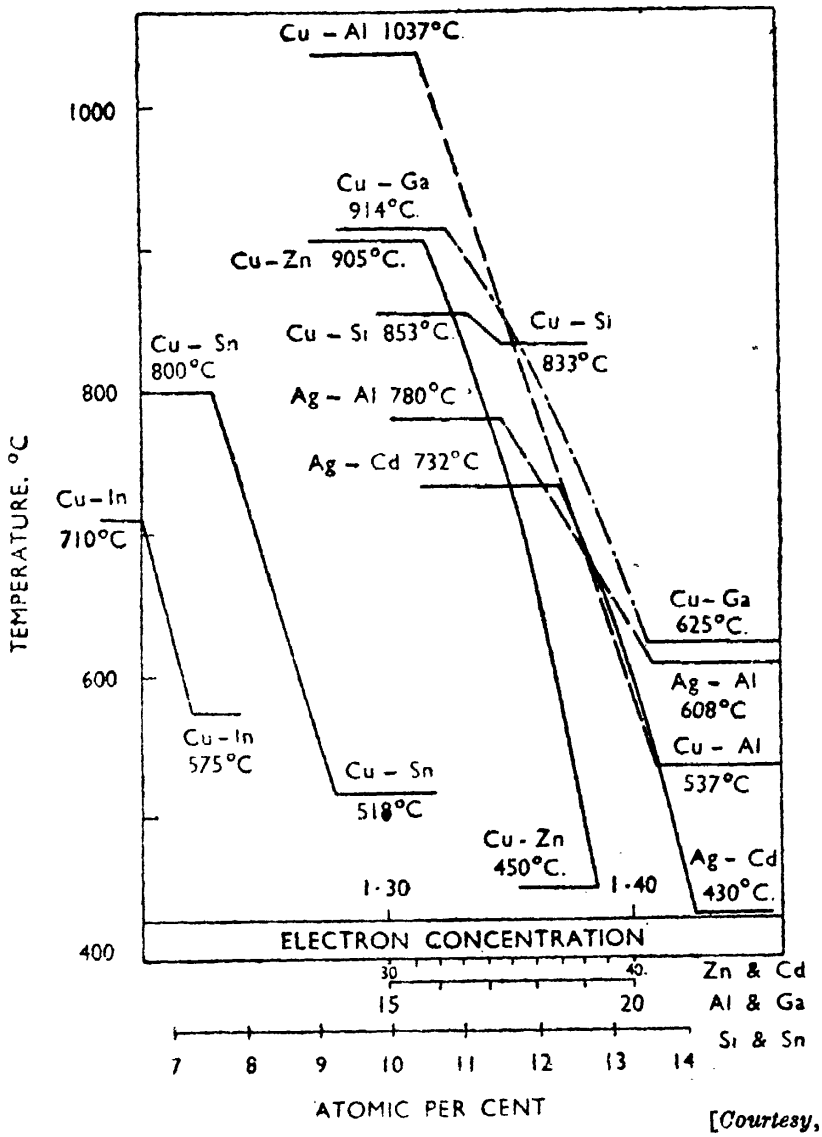
[*Courtesy Physical Society.*

FIG. 104.—The Difference between the Fermi Energies of the face-centred and body-centred cubic structures as a function of the number of electrons per atom.

shows that some mistake was made, and at present it can only be claimed that the simple electron theory indicates the approximate positions of the $\alpha/\alpha + \beta$ and $\alpha + \beta/\beta$ phase boundaries in this class of alloy. It is clear that the simple theory in which electron concentration alone is considered will only be valid in systems where the size factors are favourable. In systems where the size factors are unfavourable, we may expect additional energy terms to be introduced owing to the strains produced by fitting atoms of different sizes on to a common lattice. If we are to compare the solubility curves of different systems, we must, of course, express them first in terms of electron concentration, and Fig. 105 shows the $\alpha/\alpha + \beta$ solubility curves from a number of copper and silver alloys. It will be seen that in the systems Cu–Al, Cu–Si, Cu–Zn, Cu–Ga, Ag–Al, and Ag–Cd, the $\alpha/\alpha + \beta$ solubility curves are all roughly superposed, and these are the systems in which the size factors are favourable. The corresponding solubility curves for the system Cu–In and Cu–Sn lie at much lower electron concentrations, and in these systems the atomic diameters of indium and tin are on the

* For references see p. 239.

borderline of the favourable zone for copper. In these systems the introduction of an atom of indium or tin into the copper lattice produces a comparatively large lattice strain, and the energy associated with this strain masks the simple effects of electron concentration. We are thus at the beginning of a very interesting branch of science in which the



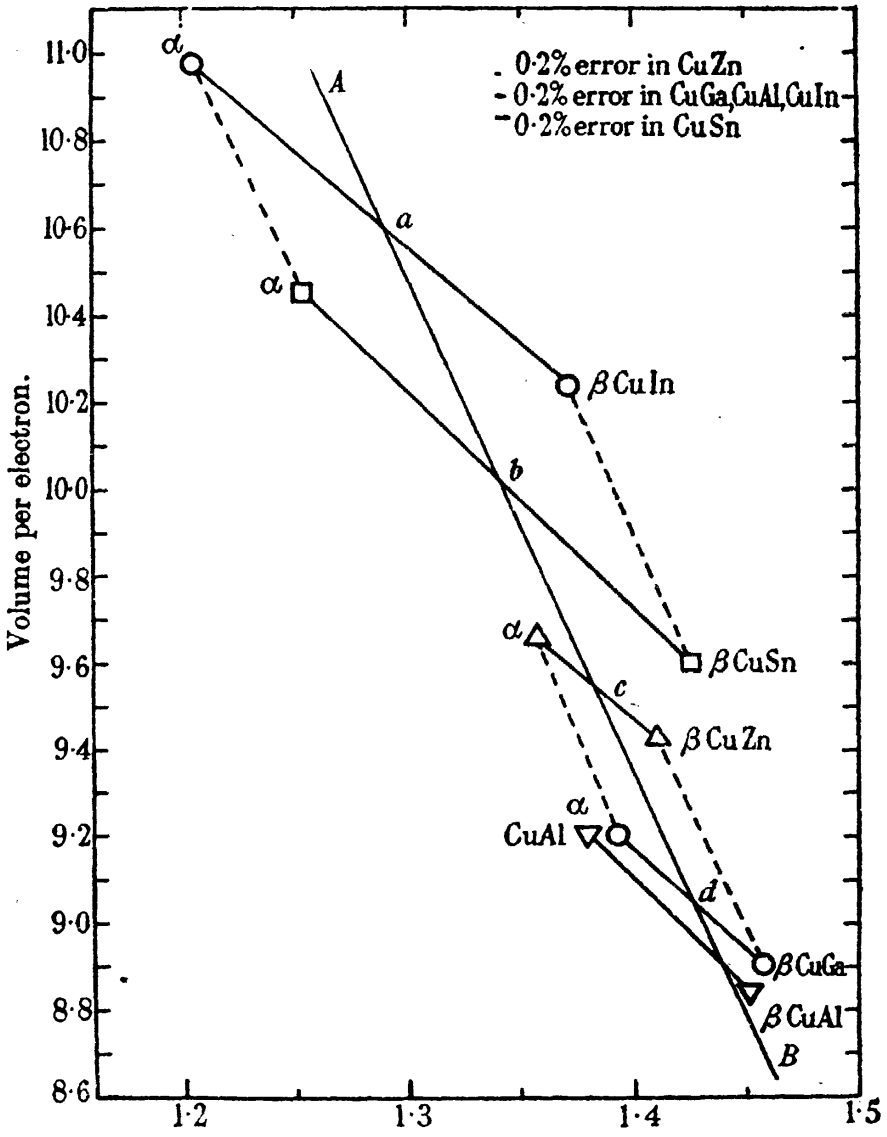
[*Courtesy, Illiffe, Ltd.*

Fig. 105.

empirical study of the facts has revealed some of the principles, and the theory will eventually have to consider the interplay of different forces.

In Fig. 43 (p. 109) it will be seen that the $\alpha/\alpha + \beta$ solubility curve undergoes a change in direction at 454° C. This is the temperature below which the β phase possesses an ordered body-centred cubic (cæsium chloride type) structure, and it is a general principle that when superlattices are formed, factors are introduced which tend to obscure the simple effects of electron concentration. This phenomenon has not yet been investigated theoretically.

The electron-concentration theory of phase boundaries thus requires extension to take into account the distortion of the lattice when one atom is substituted for another. This problem has not yet been solved theoretically, but some of the principles have been discovered empirically by high-temperature X-ray technique. In equilibria of the α/β-brass type we are concerned with two phases, and the effect



[*Courtesy Royal Society.*

FIG. 106.—In this diagram the abscissæ show the number of electrons per atom for the α (face-centred cubic) and β (body-centred cubic) phases in equilibrium with one another in the systems Cu–Zn, Cu–Ga, Cu–In, Cu–Sn, and Cu–Al, at a standard temperature of 672° C. The ordinates show the volume per valency electron as determined by high-temperature X-ray methods. The diagram shows the way in which the mean lattice distortion affects the electron concentration in the α/β brass kind of equilibrium.

of lattice distortion is likely to be revealed as a relation between the composition and lattice spacings of the two phases, rather than as an effect on one phase boundary alone. We may note that the mean lattice distortion as revealed by X-rays is not a complete measure of the distortion process concerned. Thus, in the α/β equilibria in the systems copper–zinc and copper–tin, the lattice spacings

of the α-phases in equilibrium with the β-phases at a given temperature are nearly the same, so that the mean lattice distortions of the α-phases are of the same order. But this distortion is produced by 35–40 at.-% of zinc in the system copper–zinc, and by less than 10 at.-% of tin in the system copper–tin. The distortion process is thus much more uniformly spread out in the system copper–zinc, and the data suggest clearly that a given mean lattice distortion, when distributed uniformly, affects the phase boundaries less than the same mean distortion proceeding from relatively few centres, where the local distortion must be correspondingly greater. To study this problem Andrews and Hume-Rothery measured the lattice spacings of the α and β phases in equilibrium with one another in the systems Cu–Zn, Cu–Al, Cu–Ga, Cu–In, and Cu–Sn at a standard temperature of 672° C. These results, together with the previously known equilibrium diagrams, enabled them to calculate (1) the electron concentration, *i.e.*, the number

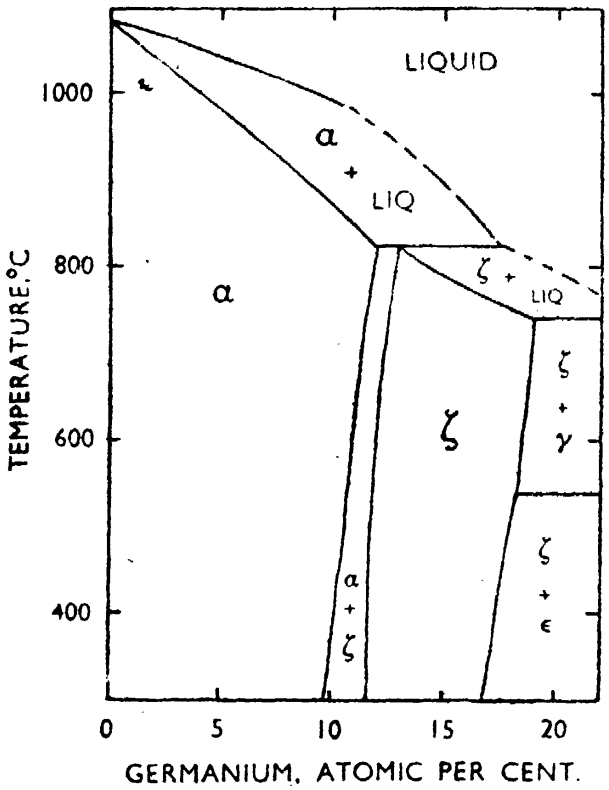


FIG. 107.—The Equilibrium Diagram of Copper-Rich Copper–Germanium Alloys. The α-phase is face-centred cubic, and the ζ-phase close-packed hexagonal. The boundaries of the α and ζ phase areas have been determined accurately, but the liquidus is uncertain beyond about 10 at.-% of germanium.

of electrons per atom, and (2) the volume per valency electron for the two phases which are in equilibrium at the temperature concerned. The results obtained are shown in Fig. 106, from which it will be seen that the electron concentrations of the two phases in equilibrium differ most greatly in the systems Cu–In and Cu–Sn, where the size-factors are most unfavourable. It will be seen that when plotted in this way, the lines joining the α and β points in each of the systems Cu–Al, Cu–Zn, Cu–Ga, Cu–In, and Cu–Sn form a series of five almost parallel straight lines, and the points *a*, *b*, *c*, *d* representing the mid-points of these lines in the systems Cu–Sn, Cu–In, Cu–Ga, and Cu–Zn lie on the oblique straight line *AB*. For these last four systems, therefore, the effect of lattice distortion on the α/β-brass equilibrium is such that at 672° C. there is a linear relation between the electron concentration and the mean volume per electron of the points lying midway between the $\alpha/(\alpha+\beta)$ and $(\alpha+\beta)/\beta$ boundaries in the equilibrium diagrams.

The data for the system copper–aluminium do not agree with this last relation, and it is to be noted that aluminium is by far the most electropositive of the

elements concerned. Examination of a large number of equilibrium diagrams has shown that there is a general tendency for the simple principles of electron concentration to be obscured when the constituents of an alloy differ greatly in electrochemical properties, and this may be regarded as the result of the electrochemical factor (p. 118).

The above examples will have shown some of the ways in which the size-factors and electrochemical factors affect this class of alloy. The theories of metals have not yet taken these factors into account, and are not yet able to explain why the electron concentration 3/2 corresponds with body-centred cubic structures in some systems only, and why this structure is replaced by β-manganese or close-packed hexagonal structures in other systems.* An empirical study of the data has, however, shown that clear relations can be traced if the equilibrium diagrams are examined systematically. Increasing valency favours the close-packed hexagonal or β-manganese structures, at the expense of the body-centred cubic structure. Thus, in the systems Cu–Zn, Cu–Ga, and Cu–Ge, the first has body-centred cubic structures only (Fig. 43, p. 109), the second has a body-centred cubic phase stable at high temperatures and a close-packed hexagonal phase at low temperatures (see Fig. 45, p. 115), whilst the last has a close-packed hexagonal phase only (see Fig. 107, p. 238). The effect of increasing valency is not always so straightforward, but can be seen in a general way in many other cases. Increasing size-factor and increasing temperature favour the body-centred cubic phase; there is no system in which a disordered body-centred cubic phase is stable at low temperatures and a β-manganese or close-packed hexagonal phase is stable at high temperatures, but there are many examples of the converse.

References and Suggestions for Further Reading.

Theory of Cohesion and Compressibility of Copper.
K. Fuchs, *Proc. Roy. Soc.*, 1935, [A], **151**, 585; 1936, [A], **153**, 622.

Theory of α/β-Brass Equilibrium.
H. Jones, *Proc. Phys. Soc.*, 1937, **49**, 250. This is the original paper and, as explained on p. 235, the work of Zener (C. Zener, *Phys. Rev.*, 1947, [ii], **71**, 846) indicates that some error has occurred as regards the effect of temperature.
K. W. Andrews and W. Hume-Rothery, *Proc. Roy. Soc.*, 1941, [A], **178**, 464.

Electron Theory of Close-Packed Hexagonal Copper–Zinc Phases.
H. Jones, *Proc. Roy. Soc.*, 1934, [A], **147**, 396.

Electron Theory of γ-Brass.
H. Jones, *Proc. Roy. Soc.*, 1934, [A], **144**, 225.

Factors Affecting the Relative Stabilities of Body-Centred Cubic, Close-Packed Hexagonal, and β-Manganese Structures in Copper Alloys.
W. Hume-Rothery, P. W. Reynolds, and G. V. Raynor, *J. Inst. Metals*, 1940, **66**, 191.

Much of the work on copper is summarized in " The Modern Theory of Solids," by F. Seitz. New York: 1940 (McGraw-Hill Book Co., Inc.).

APPENDIX.

The approximate positions of the first peaks on the $N(E)$ curves of the face-centred and body-centred cubic structures can be calculated as follows. As a first rough approximation we may assume that the electrons in the zone model have the E/k relations of free electrons, so that the Fermi surface of occupied states is a sphere whose volume is given by the equations of Chapter XV. The first peak on the $N(E)$ curve for the body-centred cubic structure occurs when the number of electrons is such that the Fermi surface just touches the Brillouin zone of Fig. 92 (p. 214). If we use the free-electron approximation, the momentum associated with electron states on the spherical Fermi surface is given by equation IV (2)

* We have already explained (p. 114) that in some systems the body-centred cubic phase is stable at high temperatures, and at low temperatures the alloy of the same composition has a close-packed hexagonal or β-manganese structure. See Fig. 45 (p. 115) for the system copper–gallium.

(p. 155), and for free electrons this momentum is equal to h/λ, where λ is the wave-length. We have, therefore, from equation IV (2):

$$\frac{4}{3}\pi p^3_{\max.} = \frac{4}{3}\pi\frac{h^3}{\lambda^3} = \frac{Nh^3}{2V}$$

and hence:

$$\lambda = \left(\frac{8\pi V}{3N}\right)^{1/3}.$$

In this way we obtain for the electron states corresponding to the first peak on the $N(E)$ curve, an expression connecting the wave-length, λ, with the number of electrons, N, in a volume, V.

We have seen in Chapter XXIII that for the electron states on the surface of a Brillouin zone, the wave-lengths satisfy the Bragg relation:

$$n\lambda = 2d\sin\theta.$$

For the body-centred cubic structure, the first Brillouin zone is a rhombic dodecahedron (Fig. 82) and the Bragg reflections are from the (110) planes of the body-centred cubic structure. The corresponding interplanar spacing, d, is equal to $\frac{a\sqrt{2}}{2}$, where a is the side of the unit cell. At the point where the Fermi sphere first touches the surface of the zone, the first-order reflection is clearly such that $n = 1$, and $\theta = 90°$ in the Bragg equation, and we may therefore write:

$$\lambda = a\sqrt{2}.$$

Now the unit cell of the body-centred cubic structure has a volume $V = a^3$, and contains two atoms, since the eight atoms at the corners are each shared with eight adjacent cells, and therefore each counts as $\frac{1}{8}$ for the particular cell considered, whilst the atom at the centre of the cell concerns the one cell alone. We may therefore write:

$$\frac{N_a}{V} = \frac{2}{a^3}$$

and

$$a = \left(\frac{2V}{N_a}\right)^{1/3},$$

where N_a is the number of atoms in volume V. It follows, therefore, that:

$$\lambda = \sqrt{2}\left(\frac{2V}{N_a}\right)^{1/3}$$

In this way a second expression is obtained for λ, involving the number of atoms N_a in volume V. On equating the two expressions for λ, we have:

$$\frac{N}{N_a} = 2^{1/2} \times \frac{\pi}{3} = 1{\cdot}48.$$

We conclude, therefore, that subject to these simplifying assumptions, the first peak on the $N(E)$ curve of the body-centred cubic structure occurs at an electron : atom ratio of 1·48.

For the face-centred cubic structure, a similar calculation may be made. In this case the unit cell contains four atoms, and we may therefore write:

$$\frac{N_a}{V} = \frac{4}{a^3}.$$

The first peak on the $N(E)$ curve for the face-centred cubic structure corresponds with the (111) reflection, for which the spacing d is equal to $\frac{a\sqrt{3}}{3}$. In this case we may therefore write:

$$\lambda = \left(\frac{8\pi V}{3N}\right)^{1/3} = \frac{\sqrt{3}}{3}\left(\frac{4V}{N_a}\right)^{1/3}$$

and

$$\frac{N}{N_a} = \frac{\pi \times 3^{1/2}}{4} = 1{\cdot}36.$$

It is thus very interesting to see how such a simple type of calculation leads to approximately correct values for the α/β phase changes in alloys of copper.

Chapter XXVIII.—Some Metals of Higher Valency.

The elements of Group II are metallic and are conductors of electricity, and they must therefore correspond with overlapping Brillouin zones, because as we have already explained (p. 197) the first Brillouin zones of simple translational lattices contain exactly two electrons per atom, and the crystals would be insulators if the zones were completely filled and no overlap occurred. Beryllium and magnesium crystallize in the close-packed hexagonal structure (Fig. 36, p. 101); the axial ratios are 1·5682 and 1·6235 respectively, and are thus very nearly that required for close-packed spheres ($c/a = 1{\cdot}6330$). For zinc and cadmium the structures are considerably elongated in the direction of the c-axis (Fig. 37), and the axial ratios are 1·8563 and 1·8859 respectively.

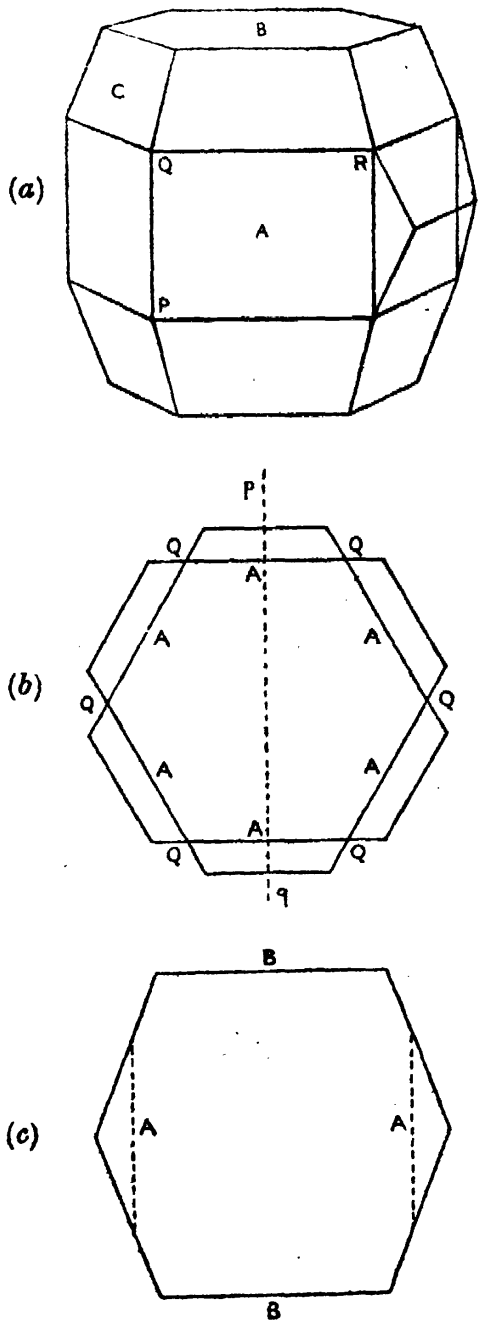


Fig. 108.—The First Brillouin Zone of the Close-Packed Hexagonal Structure.

The first Brillouin zone of the close-packed hexagonal structure, shown in Fig. 108, has certain curious characteristics. Within the volume of k-space enclosed by planes of the types A, B, and C (Fig. 108(a)), the energy varies continuously with the wave-number in all directions of k-space, and there is an energy gap across each of the bounding planes. The calculations of Jones show, however, that the energy discontinuity vanishes along certain edges such as PQ and QR, so that the smallest volume in k-space surrounded anywhere by an energy discontinuity is that enclosed by the original figure, with the addition, on each of the A faces, of a small truncated prism.*

* For this reason some writers prefer to take a larger zone as constituting the first Brillouin zone, but if this policy is adopted the first zone will contain surfaces of energy discontinuities within the zone as well as those across the boundaries.

This is shown on one of the A faces in Fig. 108(a). The shape of the equatorial section of the complete zone is shown in Fig. 108(b), whilst a vertical section along the plane pq is shown in Fig. 108(c). This complete zone, surrounded everywhere by an energy discontinuity, contains exactly two electrons per atom. The ratio of the height of the zone to the length of the side of the base varies with the axial ratio of the crystal, the variation being in the opposite direction to that of the structure of the crystal itself in real space. That is to say, in the case of zinc and cadmium, where c/a = approx. 1·9, and the crystal structure is extended in the c-direction compared with the structure for close-packed spheres, the Brillouin zone is relatively short and squat compared with the zones for beryllium and magnesium, for which c/a = approx. 1·6. The energy of an electron state at the point A is in general different from that of a state at the point B, and for the short squat zone of zinc and cadmium $E_B < E_A$, whilst with beryllium and magnesium $E_A < E_B$. Since the complete zone contains exactly two electrons, and since all four metals are conductors of electricity, there must be an overlap into a second zone, and two kinds of overlap have to be considered.

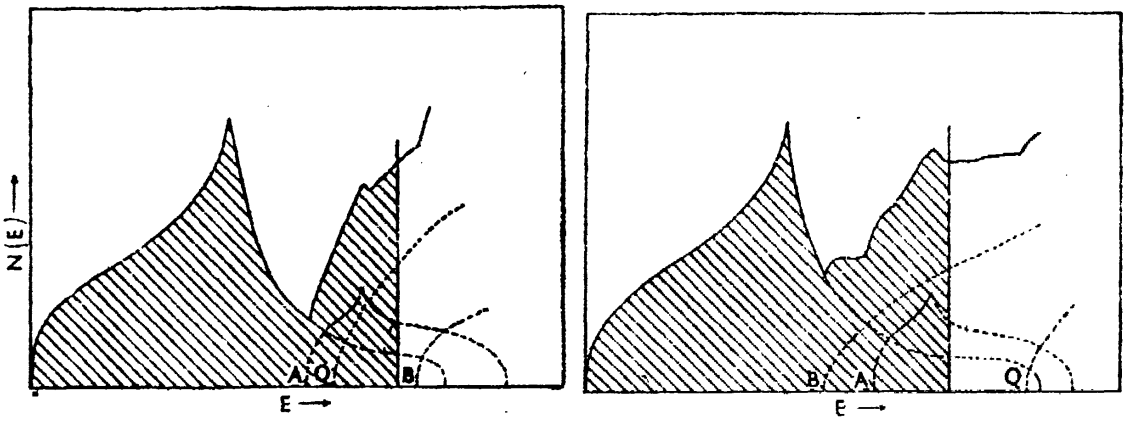
(a) Overlap from the incomplete first zone across the faces A into the small truncated prisms (Fig. 108). This will be termed the A overlap.

(b) Overlap from the complete first zone into a second outer zone. This may occur either at B in Fig. 108(a) or at the re-entrant corners (points Q in Fig. 108(b)). These may be termed the B and Q overlaps respectively, and the axial ratio is the main factor in determining which occurs first.

The calculations of Mott and Jones indicate that for beryllium and magnesium, and for other metals with an axial ratio less than 1·63, the A overlaps take place first, followed by the Q overlaps, but with two electrons per atom there is no overlap at B. For zinc and cadmium, with axial ratios of approximately 1·9, the B overlap takes place first, followed by the A overlap, but with two electrons per atom there is no overlap at Q. The axial ratio thus affects the order of the overlaps, but with electron concentrations of about 2·0, the total number of electrons outside the first zone does not depend greatly on the axial ratio.

There is an essential difference between the $N(E)$ curves for overlap into the outer zone at B and Q. The overlap at Q concerns electrons with wave numbers in six directions (perpendicular to the c-axis), whereas the overlap at B concerns electrons with wave numbers in

only two directions (parallel to the hexagonal axis). For a given energy increase, therefore, there will be more electron states available in the case of the Q overlaps than for the B overlaps and, in consequence, the $N(E)$ curve for the Q overlaps will, after the initial vertically rising

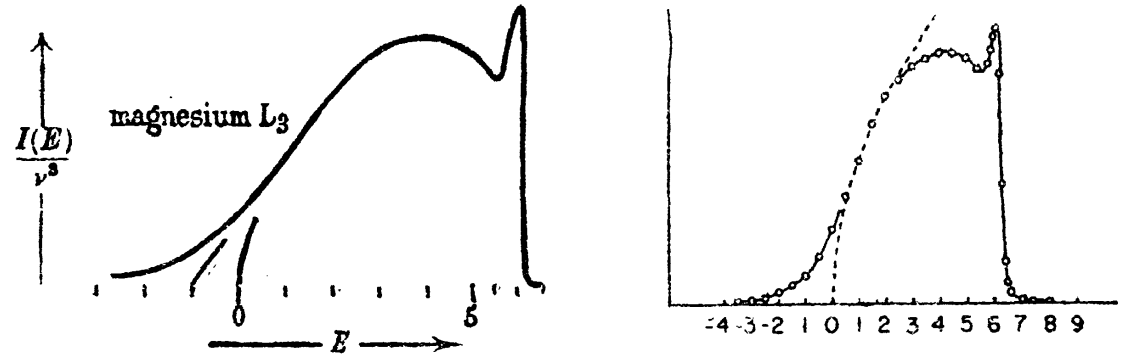


(*a*) (*b*)

FIG. 109.—$N(E)$ Curves for (*a*) Magnesium and (*b*) Zinc and Cadmium.

portion has been passed, rise more steeply away from the energy axis than that for the B overlaps.*

Accurate $N(E)$ curves are not yet available, but the general characteristics to be expected are shown qualitatively † in Fig. 109. In



Electron volts. Electron volts.

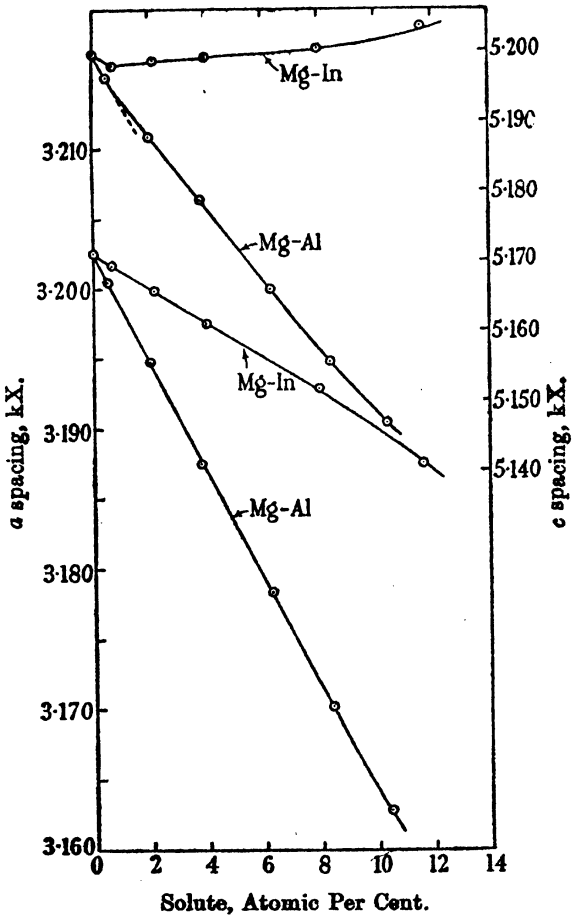
(*a*) (*b*)

FIG. 110.—*L* Emission Curves for Magnesium obtained (*a*) by Skinner (*courtesy Royal Society*) and (*b*) by Cady and Tomboulian (*courtesy Physical Review*).

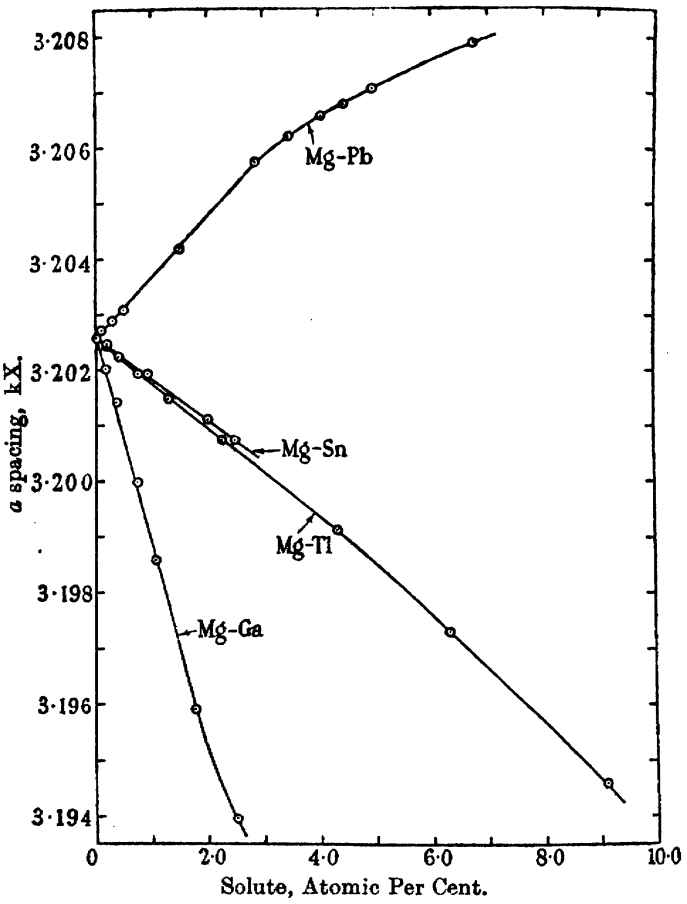
the case of magnesium, the general state of affairs is shown in Fig. 109(*a*). The A overlaps occur first, and the small A zone in Fig. 109(*a*) is that of the six small truncated prisms fitting on to the A faces of Fig. 108(*a*). The A overlap is followed by the overlaps at Q into the

* The form of the $N(E)$ curves depends, of course, on the exact details of the potential fields, but it would require an unusual configuration of the E/k curves to disturb the above general conclusions.

† These diagrams were given to us by Professor N. F. Mott, F.R.S., in 1938, and grateful acknowledgement is made to him.


Mg-In
Mg-Al
Mg-In
Mg-Al
a spacing, kX.
c spacing, kX.
3·210
3·200
3·190
3·180
3·170
3·160
5·200
5·190
5·180
5·170
5·160
5·150
5·140
0
2
4
6
8
10
12
14
Solute, Atomic Per Cent.

(*a*)


Mg-Pb
Mg-Sn
Mg-Tl
Mg-Ga
a spacing, kX.
3·208
3·206
3·204
3·202
3·200
3·198
3·196
3·194
0
2·0
4·0
6·0
8·0
10·0
Solute, Atomic Per Cent.

(*b*)

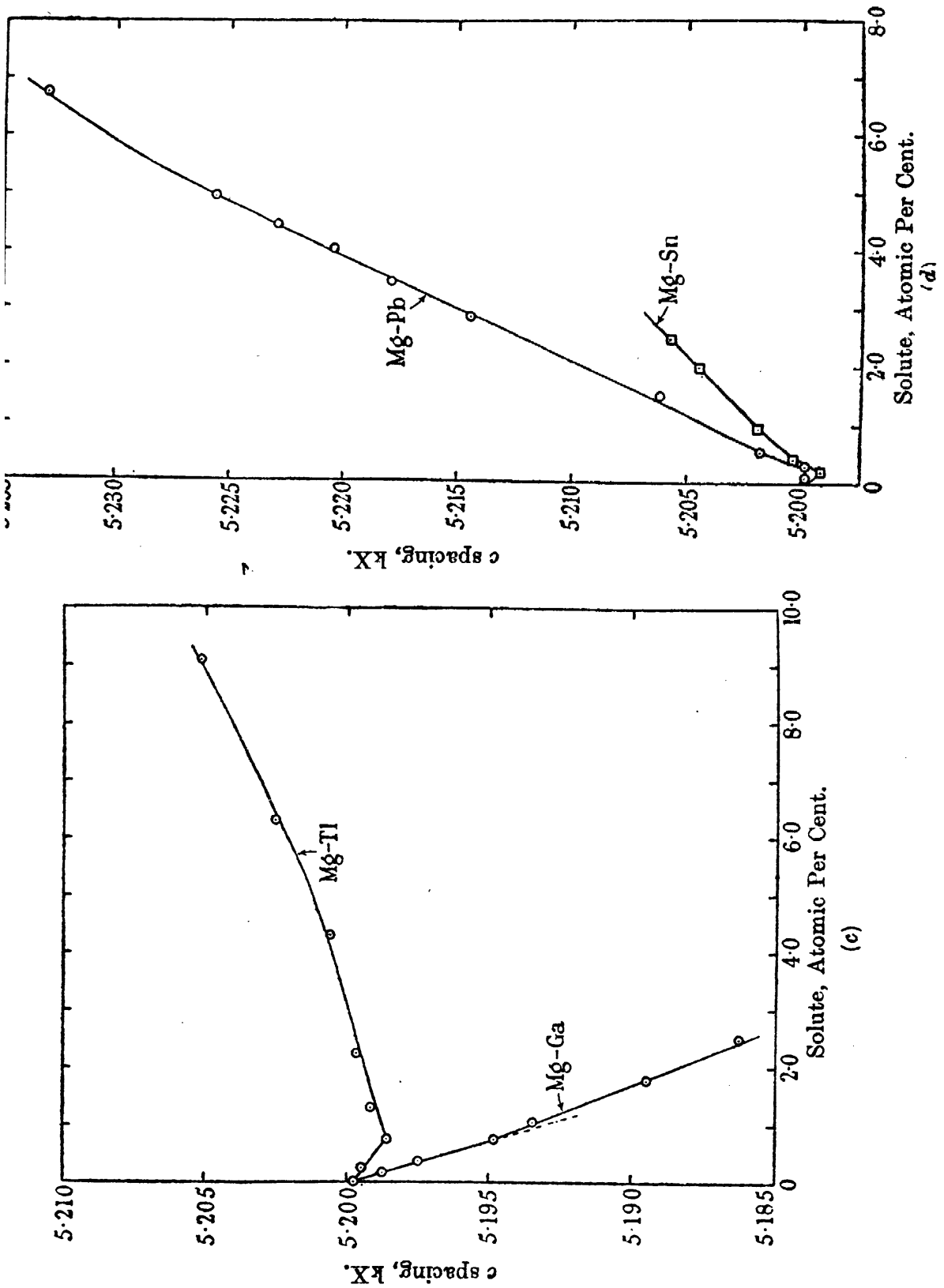


FIG. 111.—The *a* and *c* Lattice Spacings of Solid Solutions of Different Elements in Magnesium. The curves for the *a* spacings are smooth and continuous, whilst those for the *c* spacings show an abrupt change in direction at a small percentage of the solute element. This change in direction indicates the point at which an overlap occurs in the *c*-direction of the Brillouin zone (see W. Hume-Rothery and G. V. Raynor, *Proc. Roy. Soc.*, 1940, [A], **177**, 27, and G. V. Raynor, *ibid.*, 1942, [A], **180**, 107). (*Courtesy Royal Society.*)

outer zone, but with two electrons per atom there is no overlap at *B*. Fig. 110 shows the *L* emission curves for magnesium obtained by Skinner (*a*) and by Cady and Tomboulian (*b*). The presence of one kink in the curve indicates clearly that a Brillouin zone overlap has occurred, which is presumably the *A* overlap. The rise in the $N(E)$ curve is too steep to show whether there is a second overlap at *Q*.

The curves of Fig. 110 give no indication of the nearness of the Fermi surface in magnesium to the point at which the *B* overlap occurs, but information on this point may be obtained from the lattice-spacing/composition curves of alloys of magnesium with elements of higher valency. The work of Jones shows that the effect of a Brillouin zone overlap in a particular direction in *k*-space is to expand the lattice in the corresponding direction in real space. If, therefore, we alloy magnesium with an element of higher valency with which it forms a solid solution, we shall expect the *a*-parameter of the unit cell to change uniformly with the composition, because the Brillouin zone overlap has already occurred in pure magnesium. The *c*-parameter/composition curve should, however, show an abrupt change in direction at the point at which the electron concentration becomes sufficiently great for the *B* overlap to occur. Fig. 111 shows some of the lattice-spacing/composition curves for solid solutions of aluminium, gallium, indium, thallium, tin, and lead in magnesium. It will be seen that the *c*-parameter/composition curves all show a sharp change in direction after a very small addition of the solute, the change being in the direction of an expansion, as compared with the gradient before the change in direction. This may reasonably be interpreted as showing that in pure magnesium the *B* overlap has nearly, but not quite, taken place, and that the addition of as little as 1 at.-% of a trivalent solute causes the *B* overlap to occur. In contrast to this, the *a*-parameter/composition curves are smooth and continuous, in agreement with the view that both *A* and *Q* overlaps have already occurred in pure magnesium. These curves show clearly that lattice-spacing/composition relations may be profoundly altered if changing composition affects a Brillouin-zone overlap, and it follows that the apparent size of an atom in solid solution, as estimated by the extrapolation of the lattice-spacing/composition curve to 100% of the solute, may be quite different according as the particular lattice-spacing curve does or does not come immediately after a Brillouin-zone overlap. In this way it has been shown that the apparent atomic diameters of some elements when dissolved in copper or silver (no Brillouin-zone overlap), are much smaller than those estimated from extrapolations of the *a*-parameter/composition

curves of solid solutions of the same elements in magnesium where a Brillouin zone overlap is concerned.

Examination of Fig. 109 shows clearly that, whilst in magnesium the overlaps occur in the order *AQB*, the corresponding order for cadmium is *BAQ*. It is thus of great interest to examine what happens when cadmium is dissolved in magnesium. At high temperatures the two metals form a continuous series of solid solutions,* and since the atom of cadmium is somewhat smaller than that of magnesium, we shall expect that when cadmium is dissolved in magnesium both *a* and *c* parameters will decrease, provided that the zone overlaps are not affected. It is clear, however, that since there are only two electrons per atom in the whole series of alloys, and since the *B* overlap does not occur in magnesium and the *Q* overlap does not occur in cadmium, the substitution of cadmium for magnesium must eventually produce a stage at which the *B* overlap begins and the *Q* overlap dies away. From this point onwards we shall expect a marked increase in the axial ratio, since the *c*-parameter will tend to expand compared with the *a*-parameter. Fig. 112 shows the lattice spacings of magnesium–cadmium alloys at 310° C., and from this it will be seen how remarkably these expectations are fulfilled. The first substitution of cadmium for magnesium produces a decrease in both the *a* and *c* parameters, and the axial ratio is but little affected. In the region 60–70 at.-% of cadmium there is a clear change in the process, and the *c*-parameter increases rapidly, while the *a*-parameter decreases more rapidly than before. This is clearly in complete agreement with what is to be expected from the onset of the *B* overlap and the dying away of the *Q* overlap, and there is a great fascination in seeing how these curious lattice-spacing relations find a logical explanation in terms of the zone theories.

The metal magnesium thus occupies a position of great interest from the point of view of electron theory, since not only are the predictions of the zone theory fulfilled, but the extreme closeness of approach of the *B* overlap, with two electrons per atom, means that the structure is near to a critical stage. This may even affect the mechanical properties, since if small amounts of elements of higher valency are present in solid solution, the crystal may be in a state in which a zone overlap may be produced by the application of tensile stress in the direction of the *c*-axis, and curious energy relations might be involved under alternating stresses.

The preceding remarks refer to the energy characteristics of the electrons in the crystals of some of the elements of Group II, and it

* At low temperatures superlattices are formed.

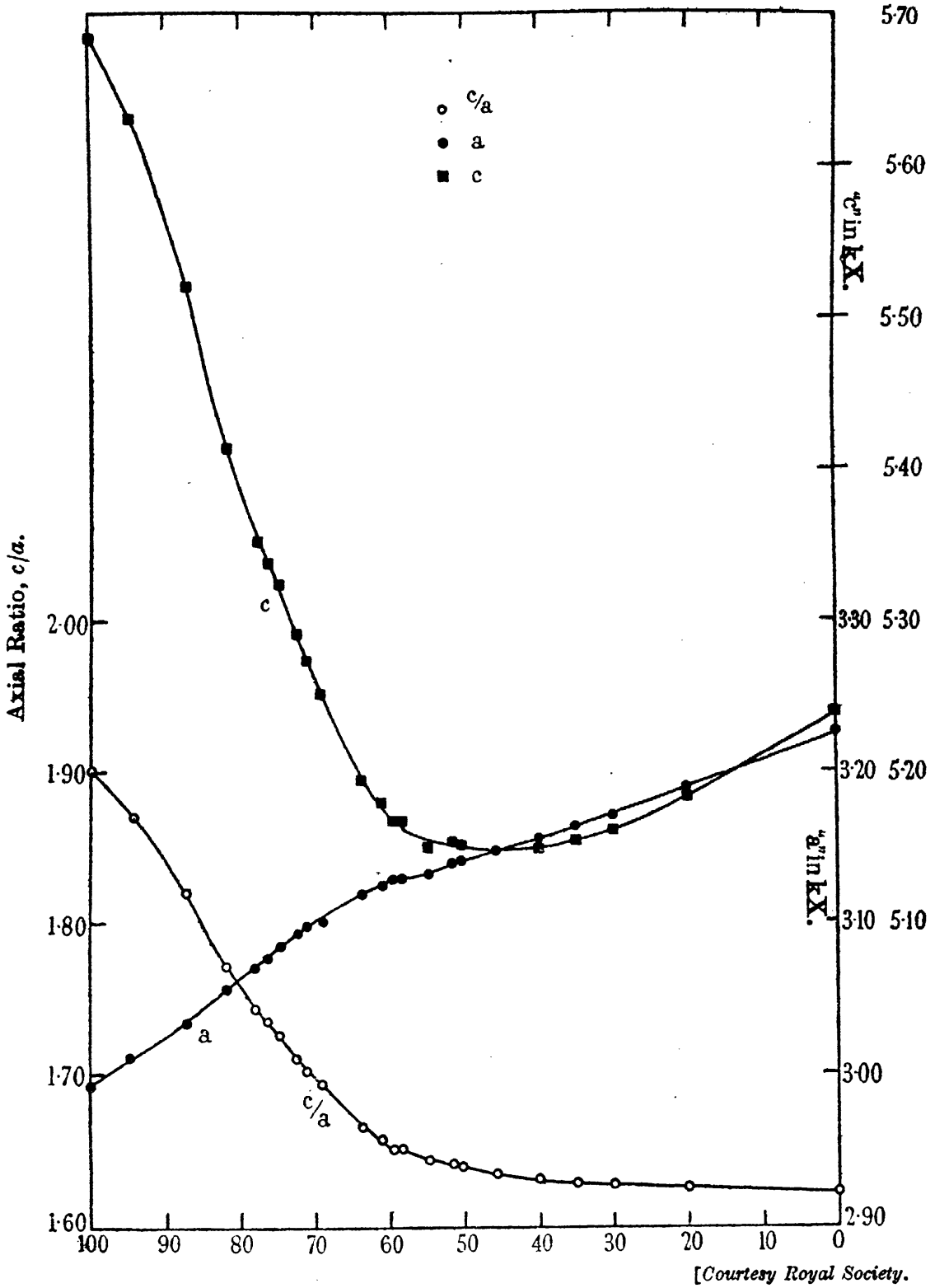


FIG. 112.—The *a* and *c* Lattice Spacings of Magnesium–Cadmium Alloys at 310° C., and also the axial ratio *c*/*a*.

remains to consider briefly the nature of their electron cloud patterns. When we compare an alkaline earth metal with the preceding alkali, we find that the alkaline earth metal has both a smaller *ion* and a smaller atomic diameter (as estimated from the closest distance of approach in the crystals of the elements). The contraction of the ion is, however, relatively smaller than the decrease in the atomic diameter, and the crystals of the alkaline earth metals are less " open " (see p. 214) than those of the alkalies. In contrast to this, when we pass from copper to zinc, silver to cadmium, or gold to mercury, the electron clouds of the underlying ions contract rapidly, whilst the atomic diameters, whether estimated from the closest distances of approach in the crystals of the elements or from the lattice distortions produced in solid solutions, increase. Zinc, cadmium, and mercury have thus more " open " structures than copper, silver, and gold. It is found that 1 at.-% of cadmium expands the lattice of copper more than does 1 at.-% of silver, and this expansion is the result of the valency electrons, because the electron cloud of the *ion* of cadmium is smaller than that of silver. This principle is quite general, and in passing down a series of elements such as

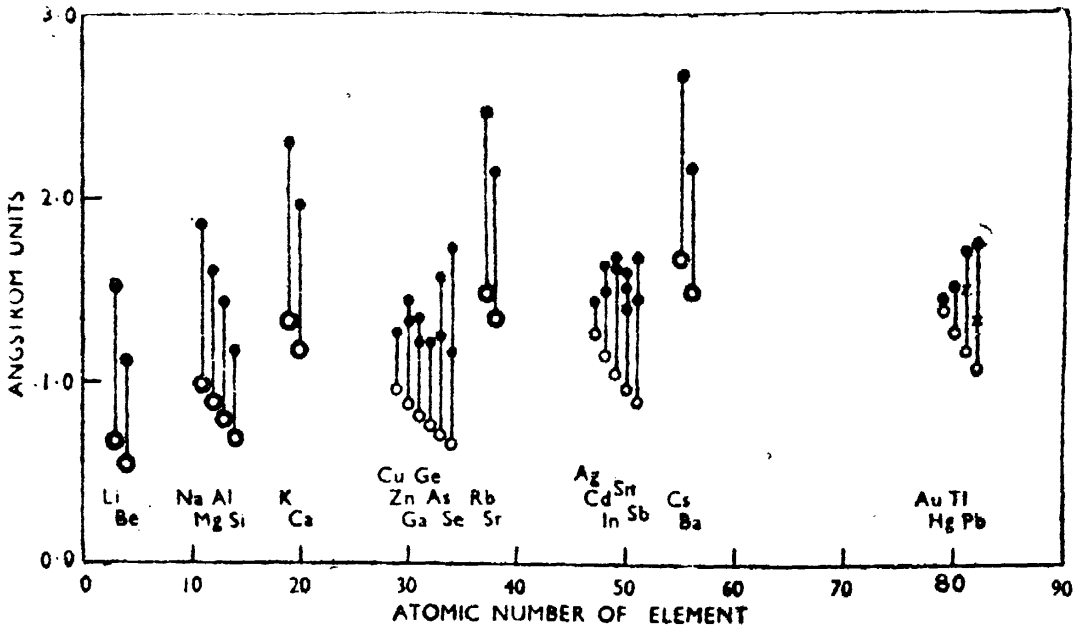
$$\mathrm{Cu} \longrightarrow \mathrm{Zn} \longrightarrow \mathrm{Ga} \longrightarrow \mathrm{Ge} \longrightarrow \mathrm{As}$$
$$\mathrm{Ag} \longrightarrow \mathrm{Cd} \longrightarrow \mathrm{In} \longrightarrow \mathrm{Sn} \longrightarrow \mathrm{Sb}$$

the underlying ion with the outer group of 18 electrons shrinks rapidly, and its electron cloud plays a continually smaller part in determining the " size " of the atom. This point is illustrated clearly in Fig. 113, which shows both the *atomic* radii and the univalent *ionic* radii of some of the elements. The variation of the electron cloud density of an ion in space cannot, of course, be adequately represented by a single number, but the univalent ionic radii of Pauling and Zachariasen * are the most satisfactory values to use when it is desired to represent the size of an ion by one constant. If the difference between the atomic

* So-called ionic radii were first deduced empirically in order to account for the interatomic distances in salts. These empirical ionic radii involve the charges on the ions, and are not measurements of the sizes of the ions if by " size " we mean the extent and density of the electron cloud. We may imagine, for example, that a univalent ion A^+ and a divalent ion B^{++} have exactly the same electron cloud pattern in free space. In an actual ionic crystal, the double charge on the B^{++} ion would result in its being pulled more strongly towards a given anion than the univalent A^+ ion would be at the same distance. The interatomic distances in salts would thus indicate a smaller ionic radius for the B^{++} ion than for the A^+ ion, even though in free space their electron cloud densities were the same. The so-called univalent ionic radii are attempts to express ionic radii free from this complication, and this work is due to Pauling (*J. Amer. Chem. Soc.*, 1927, **49**, 765) and Zachariasen (*Z. Krist.*, 1931, **80**, 137). The electron cloud density of an ion in space cannot, of course, really be represented by a single number, but where one constant has to be used, the univalent ionic radii of Pauling and Zachariasen are the most satisfactory.

radius (*i.e.*, one-half the closest distance of approach in the crystal of the element) and the ionic radius is looked on as a measure of the degree of "openness" of a metal, Fig. 113 shows clearly how the metals following an alkali metal become progressively less open with increasing valency, whilst in the elements following copper and silver the structures become progressively more open.

The rapid contraction of the ions in the elements following copper and silver leads to interesting solid-solubility relations in cases where the electron clouds of the ions are concerned in the process. When,



[*Courtesy Philosophical Magazine.*

FIG. 113.—Atomic Radii and Univalent Ionic Radii of the Elements.

KEY.

● ½ (interatomic distance in the crystal of the element).
◎ Zachariasen univalent ionic radii.
○ Pauling univalent ionic radii.
× Goldschmidt empirical ionic radii.

for example, silver, cadmium, indium, tin, or antimony is dissolved in solid copper, the mean lattice distortions produced by 1 at.-% of the above elements are in the order :

$$\text{Ag} < \text{Cd} < \text{In} < \text{Sn} < \text{Sb}.$$

Now when the size-factors are favourable and the electrochemical factor is small, we have seen (p. 235) that the maximum solid solubilities of the above elements in a univalent face-centred cubic solvent are of the order :

$$100 : 40 : 20 : 12 : 7\text{–}8,$$

since the univalent elements should mix completely, whilst the remaining elements dissolve up to a limit which corresponds to an electron

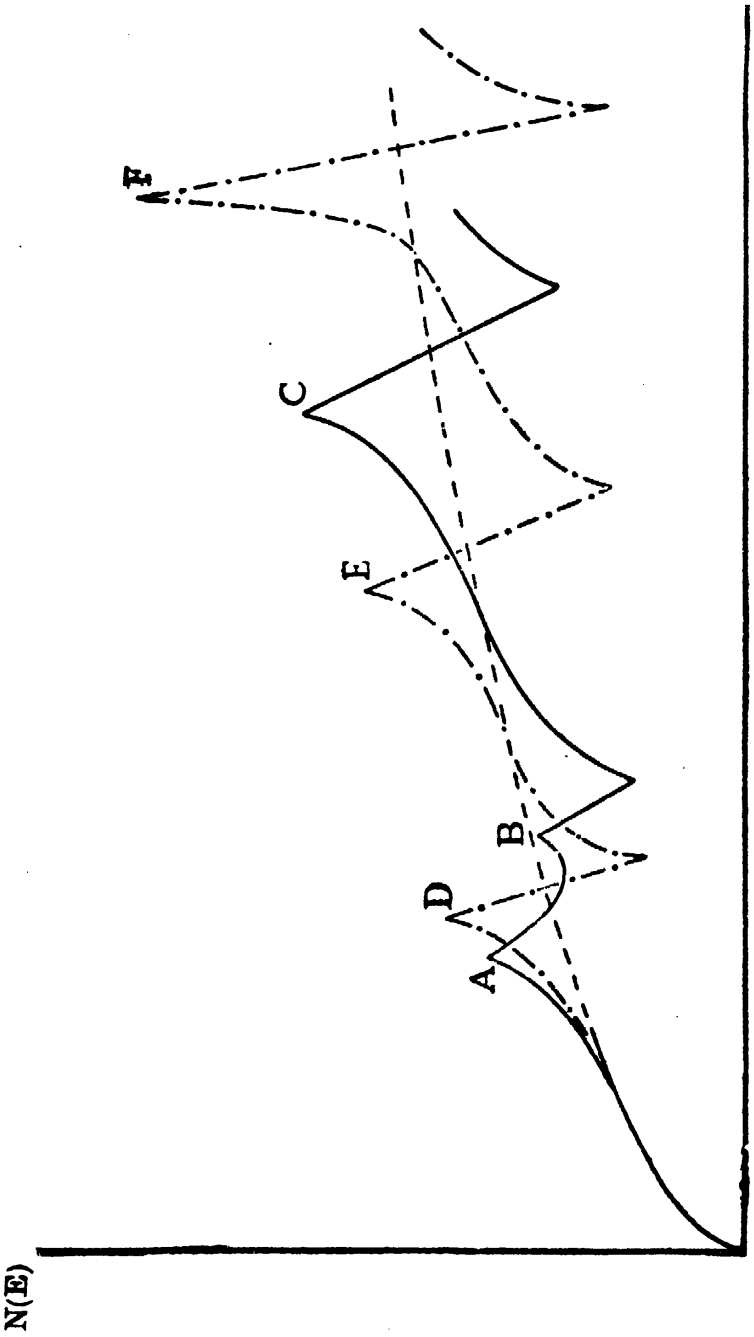
concentration of the order 1·4. The maximum solid solubilities of the above elements in copper are as follows:

Ag.	Cd.	In.	Sn.	Sb.
5·4	1·7	10·9	9·3	5·9

From these figures it will be seen that the solid solubilities of indium, tin, and antimony in solid copper approach more nearly to the normal values than do those of silver or cadmium, in spite of the fact that the mean lattice distortion per atom increases with the valency of the above solutes. We have thus the curious position that the mean lattice distortion of copper produced by one atom of indium is greater than that produced by one atom of cadmium, but that at the same time it is more easy for the atom of indium to enter into solid solution in copper. The reason for this effect is almost certainly the rapid shrinking of the *underlying ion* which takes place with increasing atomic number of the above solutes. In the case of silver, as can be seen from Fig. 113, the atomic and ionic radii are of the same order, with the result that the introduction of the silver atom into the copper lattice involves the dense electron cloud of the silver ion. On passing to cadmium, indium, tin, and antimony, the underlying ions shrink rapidly, and their electron clouds play a diminishingly important part in the process, with the result that the solid solubilities approach more nearly to their normal values. This example serves to illustrate the dangers of attempting to represent the size of an atom by a single constant, and shows that in some cases it is necessary to consider not merely the characteristics of the valency electrons, but also those of the outermost shell of the ions.

We have seen that in the crystals of the divalent elements there is always an overlap from the first Brillouin zone, and with trivalent elements it is obvious that considerable overlapping must take place. Fig. 29 (p. 92) shows the L_3 emission curve for aluminium as determined by Skinner, and this clearly shows signs of two overlaps. The first calculation of an $N(E)$ curve for the face-centred cubic structure was made by Mott and Jones, whose curve is shown by the full line in Fig. 114. In this work the energy gap at the surface of the first Brillouin zone was deduced from the optical properties of copper, and the points A and B represent the stages at which the Fermi surface touches the octahedral and cube faces of the zone respectively.* The deep trough after B represents the stage at which the overlap occurs across the (111) octahedral faces of the zone. The remainder of the curve is very speculative, and the (200) overlap is not shown. It will be appreciated that the relative positions of the later peaks and valleys depend on the

* See Fig. 75 for the shape of the zone.



[*Courtesy Royal Society.*

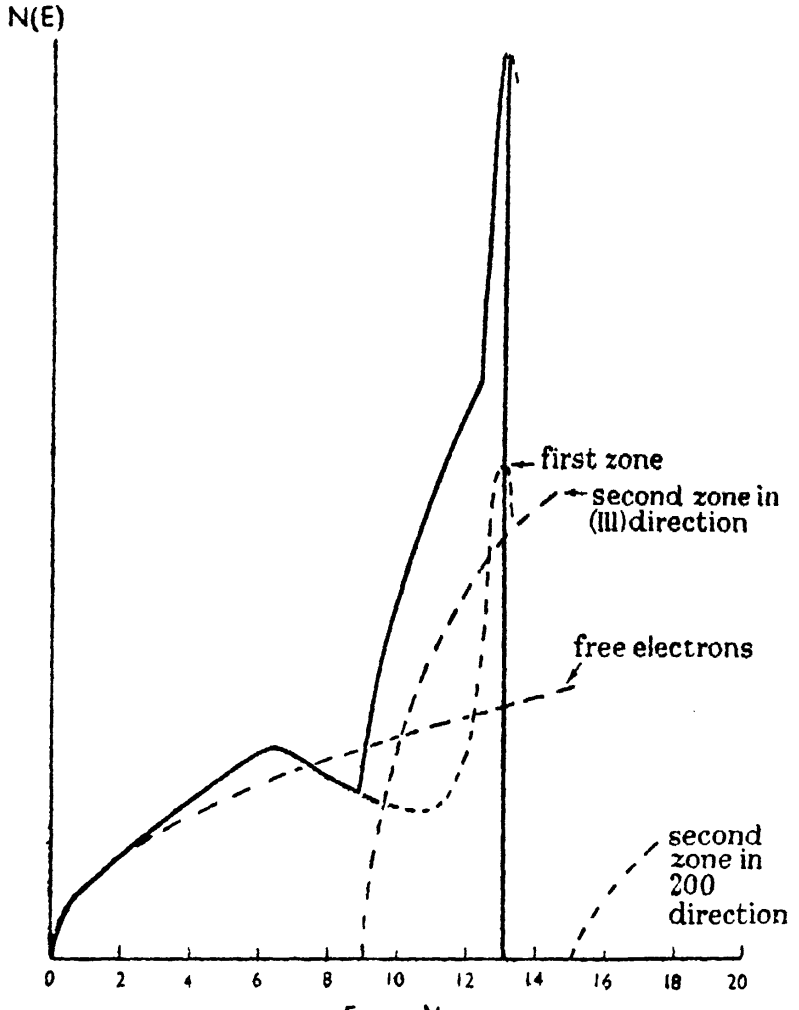
FIG. 114.—Density of States in Body- and Face-Centred Cubic Metals.
- - - - - - Free electrons.
——— Face-centred cubic lattice.
- . - . - . Body-centred cubic lattice.

The peaks *A*, *B*, *C* arise from the planes (111), (200), (220), respectively, and *D*, *E*, *F* from the planes (110), (200), (211), respectively. In the curve for the face-centred cubic structure, the peaks *A*, *B*, and *C* occur at electron : atom ratios of 1·36, 2·10, and 5·9, respectively. In the curve for the body-centred cubic structure, the peaks *D*, *E*, and *F* occur at electron : atom ratios of 1·48, 4·21, and 7·7, respectively.

It will be appreciated that the relative positions of the various peaks and valleys depend on the magnitudes of the energy gaps at the zone boundaries. The curves in the Figure are calculated on the assumption that the energy gaps are equal to those deduced for copper from its optical properties. The high energy portions of the curves are speculative, and the curve for the face-centred cube does not show the (200) overlap.

magnitude of the energy gaps which are assumed, and this part of the curve cannot, therefore, be used for critical comparison with facts.

The $N(E)$ curve for aluminium has recently been worked out more accurately by Matyas * who took into account the symmetry of the s and p functions of the valency electrons. The $N(E)$ curve obtained in this work is shown in Fig. 115. In the diagram the full line shows the total $N(E)$ curve. The first peak represents the stage at which the Fermi surface first touches the (111) or octahedral faces of the zone, and the bottom of the first trough is where the overlap begins across these



[*Courtesy Royal Society.*

FIG. 115.

(111) faces. The symmetry of the p functions has the curious effect that on further increasing the number of electrons per atom, the occupied states do not spread out so as to touch the centres of the cube (200) faces of the zone as was the case at point B in Fig. 114 for the simple model of Mott and Jones. Instead of this the occupied states spread out so that at 3 electrons per atom the first zone is very nearly but not quite filled, the remaining unoccupied states lying in thin slabs

* Work not yet published.

parallel to the (200) faces of the zone. As the first zone contains 2 electron states per atom and is not quite filled, it follows that slightly more than 1 electron per atom has passed into states in the second zone. According to the work of Matyas, aluminium is thus an element in which the first zone is very nearly filled, and there is slightly more than 1 electron per atom in the second zone. The state of affairs is quite different from that suggested by the curve of Fig. 114, and this serves to illustrate the point emphasized on p. 212 that when the symmetry of the p or d functions is taken into account the order of overlaps and shapes of the Fermi surface may be quite different from those of the simple zone theories.

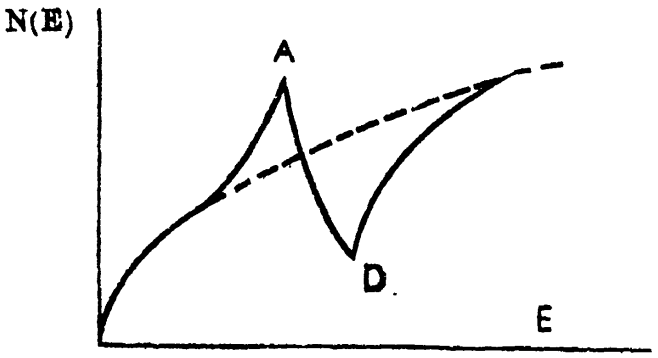
From Fig. 115 it will be seen that the $N(E)$ curve for aluminium rises to a sharp narrow peak which is in the region of 3 electrons per atom, and this may be connected with the fact that the solubility of most elements in solid aluminium is very restricted. For the substitution of atoms of higher or lower valency will alter the electron concentration so that the latter corresponds to a lower position on the $N(E)$ curve, and hence to a structure which becomes relatively less stable compared with other possible structures whose $N(E)$ curves remain high. Actually the various equilibrium diagrams suggest that at low temperatures no element forms an appreciable solid solution in aluminium, whilst at high temperatures zinc is the only element whose solubility exceeds 20 atomic per cent. There is, however, no obvious reason why the trivalent elements gallium and indium do not form wide solid solutions in aluminium.

In many alloys of aluminium it is found that the apparent size of the aluminium atom in the alloy is smaller than that indicated by the interatomic distances in the crystal of the element, and much discussion has taken place as to the reason for the contraction which occurs in the alloys. In some cases it is probably due partly to the electropositive nature of aluminium, which gives rise to a relatively large electrochemical factor. This explanation by itself does not cover all the facts, and much of the contraction is probably due to the interatomic distances in pure aluminium being expanded as the result of the Brillouin-zone overlap. If the aluminium atom finds itself in an alloy where no zone overlap is concerned, this expansion no longer takes place, and consequently the apparent size of the atom is smaller. In this way it has been possible to show that when aluminium is dissolved in copper or silver, where there is no zone overlap, the apparent size of the aluminium atom as estimated from the lattice-spacing/composition curve is about 2·71 A., and is thus considerably smaller than the interatomic distances in the crystal of aluminium (2·86 A.). On the other hand, when

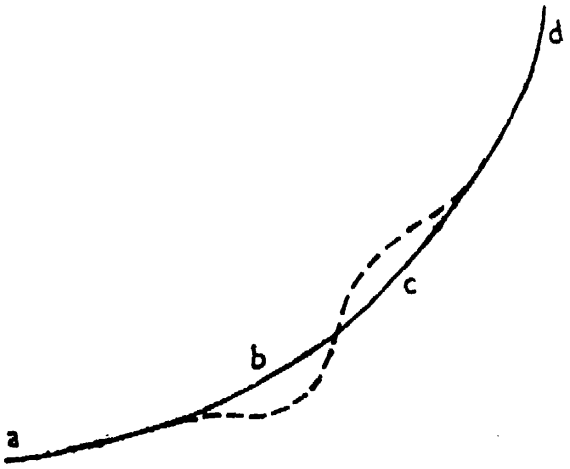
aluminium is dissolved in magnesium, where a Brillouin-zone overlap has occurred in the direction perpendicular to the hexagonal axis, the apparent size of the aluminium atom as estimated from the interatomic distances in the direction of the overlap is about 2·83–2·84 A., and is thus large and of the same order as that in the crystal of the element. These examples show in a very elegant way how the apparent sizes of atoms are affected by Brillouin-zone overlaps.

From Figs. 114 and 115 it will be appreciated that $N(E)$ curves may be found with very sharp peaks and valleys. We may consider a simplified $N(E)$ curve such as that of Fig. 116, where there is a sharp peak at A and a deep trough at D. Then, as previously described, we shall in general expect an alloy whose electron concentration corresponds to the trough D to take up an alternative structure with a higher $N(E)$ curve. If, however, there is no such alternative structure the interesting possibility arises that at the electron concentration of the trough, the alloy will be more stable as a mixture of two constituents * each of the same structure but of different compositions than as a single uniform phase. This can be understood from Fig. 116 (*b*), where the full curve shows the relation between the total energy and the number of electrons in an electron gas, whilst the dotted line shows the corresponding curve for the Brillouin-zone model which gives rise to the $N(E)$ curve of Fig. 116 (*a*). In Fig. 116 (*b*) the portion *b*, where the dotted line sinks below the full curve, corresponds with the region of the peak A on the $N(E)$ curve since the high $N(E)$ curve means that a given number of electrons can be accommodated with a relatively low energy. Conversely the portion *c*, where the dotted line rises above the full line, corresponds with the region of the trough D in the $N(E)$ curve. It is clear that this type of curve means that at some region in the neighbourhood of *c* a single phase of one composition will have a higher energy than a mixture of the two phases of higher and lower electron concentrations, since a tangent can be drawn across the curve and lies below the curve itself. It is thus possible that an $N(E)$ curve with a deep trough may result in a single solid solution splitting up into two congruent solid solutions of the same crystal structure but of different compositions. This effect is, in fact, found to occur in the system aluminium–zinc where at high temperatures there is a wide solid solution of zinc in aluminium which separates into two congruent solid solutions at lower temperatures. It was originally thought that this might be the result of a trough in the $N(E)$ curve, since the deep trough after the peak at B in Fig. 114 occurs

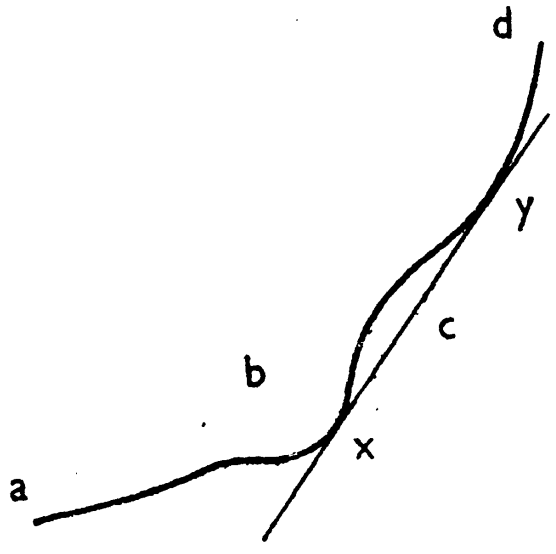
* Objection may be taken to the use of the word constituent here. There seems to be no accepted term to describe an alloy consisting of crystals of two kinds each of the same structure but of different composition. The phenomenon is analogous to the splitting up of a liquid solution into two congruent (immiscible) liquids.



(*a*)



(*b*)



(*c*)

FIG. 116.

at roughly the correct electron concentration. The work of Matyas (Fig. 115), however, shows clearly that the original curve of Mott and Jones (Fig. 114) is very much over-simplified, and it is not possible to apply the argument to the system aluminium–zinc until the $N(E)$ curve has been calculated for a face-centred cubic lattice consisting of a mixture of zinc and aluminium atoms. The general argument based on Fig. 116 is correct for the condition of affairs at the absolute zero, and at higher temperatures the same general argument may be applied, except that the criterion for the equilibrium structure is that the free energy F is a minimum, where F is defined by the relation

$$F = U - \theta S$$

where U is the total internal energy, θ the absolute temperature, and S the entropy. At the absolute zero the condition is thus that U is a minimum which is the simple argument described above in connection with Fig. 116.

REFERENCES AND SUGGESTIONS FOR FURTHER READING.

Electron Theory of Magnesium, Cadmium, and Close-Packed Hexagonal Lattices.

N. F. Mott and H. Jones, "The Theory of the Properties of Metals and Alloys." Oxford: **1936**, p. 161 (Clarendon Press).

H. Jones, *Proc. Roy. Soc.*, 1934, [A], **144**, 225.

W. Hume-Rothery and G. V. Raynor, *J. Inst. Metals*, 1938, **63**, 227.

Lattice-Spacing Relations in Solid Solutions in Magnesium.

W. Hume-Rothery and G. V. Raynor, *Proc. Roy. Soc.*, 1940, [A], **177**, 27.

This paper describes the work showing how the apparent sizes of atoms in solid solution are affected by Brillouin-zone overlaps.

G. V. Raynor, *ibid.*, 1942, [A], **180**, 107.

W. Hume-Rothery and G. V. Raynor, *ibid.*, 1940, [A], **174**, 479 (Mg–Cd alloys).

Effect of Ionic Radius on Solid-Solubility Relations.

W. Hume-Rothery and G. V. Raynor, *Phil. Mag.*, 1938, [vii], **26**, 143.

Chapter XXIX.—The Elements of the First Long Period.

(1) *General.*

On passing from potassium to bromine, the elements of the First Long Period show the sequence of changes associated with the transition process in which the 3*d* sub-group is built up, followed by the gradual development of electronegative properties in the elements of the B sub-groups. Additional interest in this series of elements is due to the appearance of ferromagnetism in iron, cobalt, and nickel.

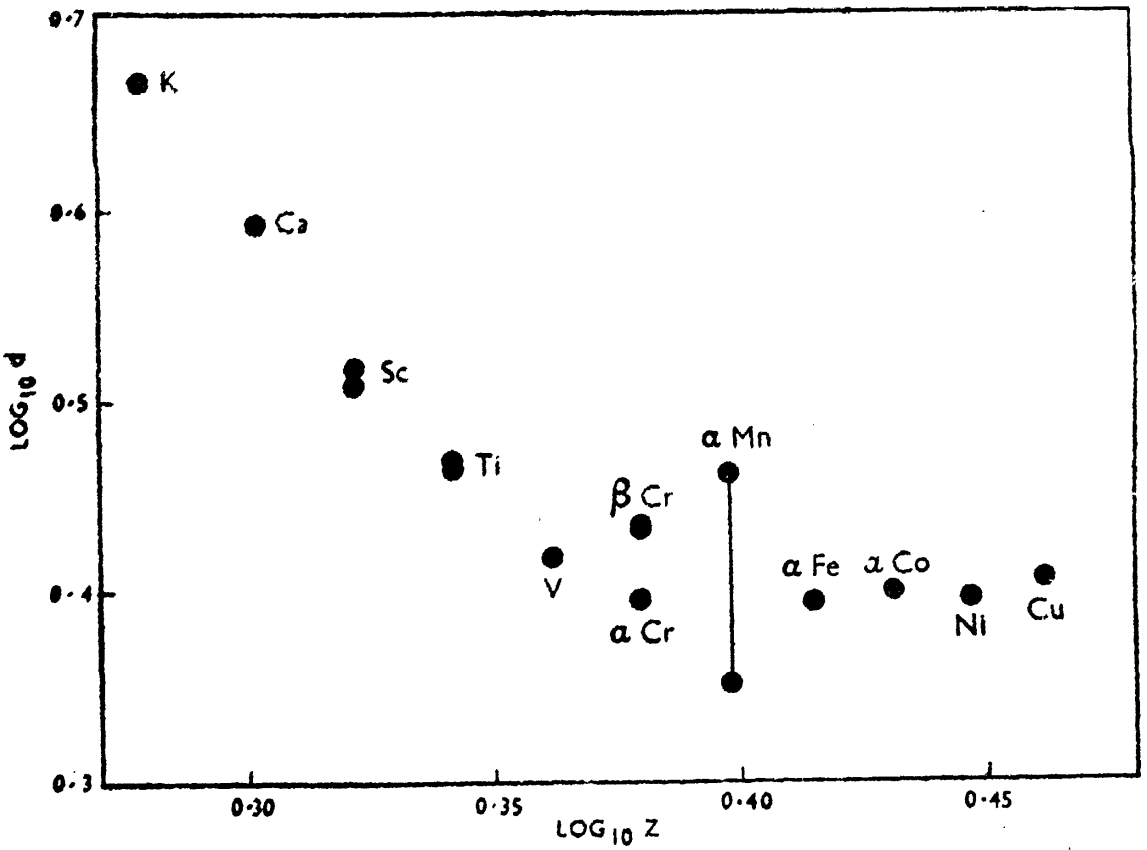


Fig. 117.—Interatomic Distances in Crystals of Elements Plotted Against Atomic Numbers (Log Scale). The structure of manganese is complicated and the line in the figure represents the range of distances that exists.

We may deal first with the crystal structures and interatomic distances in the crystals of the elements. From potassium to copper the elements show the typical metallic structures, face-centred cube, body-centred cube, and close-packed hexagonal, with the exception of manganese which crystallizes in two very complicated structures. The interatomic distances in this series of elements are shown in Fig. 117, in which $\log_{10} d$ is plotted against $\log_{10} Z$, where Z is the atomic number

and d is the closest distance between two atoms in the crystal structure of the element. It will be seen that there is a rapid fall in the atomic diameter * on passing from potassium to vanadium, and then a less rapid fall on passing to chromium and manganese, after which the atomic diameter shows a slight increase. Fig. 118 shows the melting points of these elements, and of the elements between tantalum and platinum in the third Long Period. From this figure it will be seen that there is a rise to a maximum in Groups VI–VII, where the interatomic distances are least. This is a general characteristic, and in all

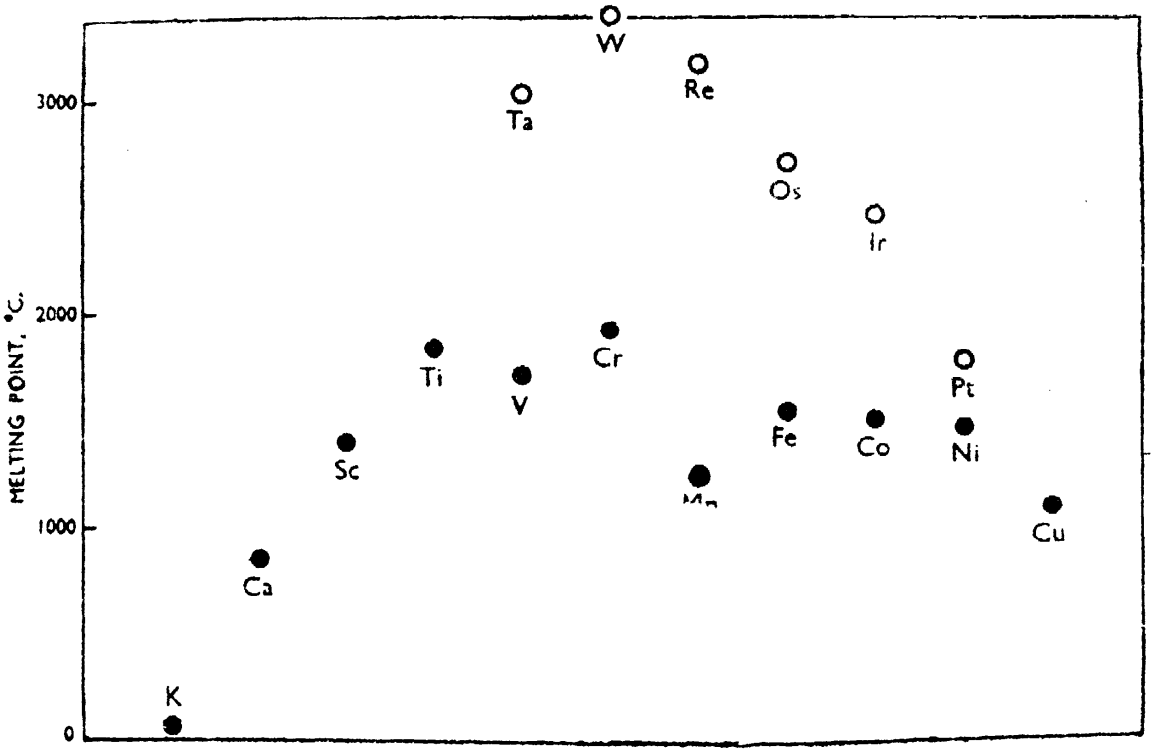


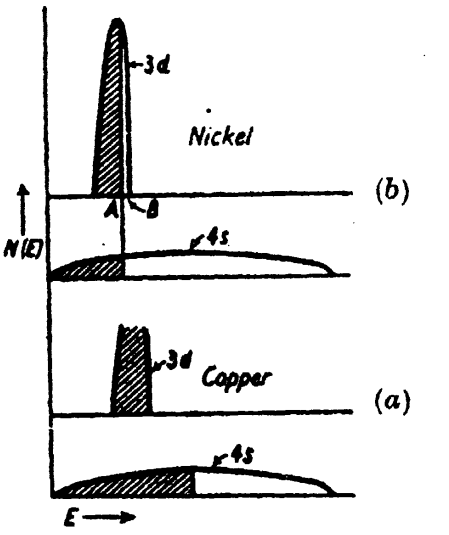
FIG. 118.—Melting Points of Elements.

three Long Periods the strength of binding in the solid clearly reaches a maximum in the region of Group VI–VIII. These transitional elements are characterized by abnormally high electrical resistances and specific heats, whilst in the First Long Period ferromagnetic properties occur in Group VIII. It is also to be noted that the elements in Groups IVA and VA (Ti, V, Zr, Nb, Hf, Ta) are supraconductors, whilst supraconductivity is not shown by the elements of Group VIA. The supraconductivity thus disappears at the point where the atomic diameters begin to decrease less rapidly.

* For convenience we use the term atomic diameter to denote closest distance of approach of the atoms in the crystals of the elements.

(2) *The Theory of Mott and Jones.*

Up to the present, no model or theory has succeeded in accounting for all the above characteristics of the transition metals. The most simple model proposed is that of Mott and Jones, who regard the outermost electrons in the transition elements of the First Long Period as being in two bands derived from the (3*d*) and (4*s*) states of the free atoms; the transition elements of the later Periods are regarded similarly as derived from *d* and *s* states with the appropriate quantum numbers. The *d*-band contains 10 electrons per atom, and the *s*-band only two, and a number of facts confirm the conclusion that the density of states in the *d*-band is much higher than that in the *s*-band, so that the $N(E)$ curves for the two bands are of the general shapes shown in Fig. 119. In copper, the *d*-band is completely filled and the position is as shown in Fig. 119(*a*), where the complete subgroup of ten $(3d)^{10}$ electrons forms part of the Cu^+ ion. In solid nickel, the *d*-band is not completely filled, and the position is as shown in Fig. 119(*b*). The number of unoccupied states in the *d*-band is equal to the saturation intensity of magnetization expressed in Bohr magnetons per atom, and the numbers determined experimentally are :



[*Courtesy Clarendon Press.*

FIG. 119.—Density of States in Nickel and Copper.

Fe 2·2	Co 1·7	Ni 0·6

The numbers of electrons per atom to be divided among the 3*s*, 3*p*, 3*d*, and 4*s* states are 16, 17, and 18 for iron, cobalt, and nickel respectively, and hence, since the $(3s)^2(3p)^6$ sub-groups are completely filled, the number of electrons per atom in 4*s* states will be :

$$\text{Fe } 16 - 8 - (10 - 2{\cdot}2) = 0{\cdot}2$$
$$\text{Co } 17 - 8 - (10 - 1{\cdot}7) = 0{\cdot}7$$
$$\text{Ni } 18 - 8 - (10 - 0{\cdot}6) = 0{\cdot}6$$

It will be noted that these numbers are not integers, and are different from the numbers of electrons in the 4*s* states of the free atoms (Table II, pp. 54–56). These results are to be interpreted as indicating that for nickel, in the crystal as a whole, there are on the average 0·6 electrons per atom in *s* states. If, instead of thinking of the crystal as a whole, we consider the electron clouds round the individual ions,

Mott and Jones show that the general tendency is for an ion to have either a complete sub-group of ten *d* electrons, or to have *two d* electrons missing, with the formation of an incomplete $(3d)^8$ group, and that there are comparatively few ions with one *d* electron missing to form a $(3d)^9$ group. In ions with the $(3d)^8$ grouping, the two "holes" in the *d*-shell (*i.e.*, the unoccupied states) have the same spin. The picture presented is not one in which an individual ion is permanently in a $(3d)^8$ state, but rather one in which there is a continual interchange of electrons in such a way that there is a very much greater chance of an ion being temporarily in a $(3d)^8$ state than in a $(3d)^9$ state. For those periods during which the nickel ion is in the $(3d)^8$ state it will act as a positive ion, and attract the valency electrons in its neighbourhood, and Mott and Jones regard this additional attraction as one of the causes of the high binding energies of the transition elements.

In Mott and Jones's model the electrical conductivity of the transition elements is due mainly to electrons in *s*-states, and the abnormally large resistance is regarded as due to the high $N(E)$ curve for the electrons in *d*-states, since as we have already explained (p. 204) this gives a high probability of electrons being scattered so as to undergo $s \longrightarrow d$ transitions which do not occur in the univalent metals.

The general conclusion of Mott and Jones that there are 0·6 "holes" in the *d*-shell of nickel has found support from a number of facts in connection with the properties of solid solutions of different elements in nickel. In brief, it may be said that if elements such as copper, zinc, aluminium, and tin are assumed to contribute their normal quota of valency electrons per atom (Cu 1, Zn 2, Al 3, Sn 4), then when these elements are dissolved in solid nickel, a number of the physical properties are accounted for if *all* of the valency electrons of the solute atoms enter the 3*d* shell of the nickel atoms. Thus the curves showing the variation of magnetic susceptibility with composition indicate that the saturation moment is decreased by 1, 2, 3, and 4 Bohr magnetons each time a nickel atom is replaced by an atom of copper, zinc, aluminium, or tin, respectively. In the copper–nickel alloys, where a continuous series of solid solutions is formed, the susceptibility becomes zero at 60 at.-% of copper. We have already seen (p. 260) that in metallic nickel at any instant there are on the average 0·6 holes per atom in the *d*-shell, and the picture presented is that the copper atoms replace those nickel atoms with the $(3d)^{10}$ sub-groups, and add one additional valency electron, so that when 60% of the nickel atoms have been replaced there are sufficient additional electrons to fill the incomplete *d*-shells. Many other properties (*e.g.*, reflective power,

lattice spacings) show variations with composition which change at 60 at.-% of copper, and thus confirm the general concept.

In the theory of Mott and Jones, the cohesion is regarded as due to the *s*-electrons, supplemented by the partly ionic forces referred to above. The great defect of the theory is that it gives no reason for the steep fall in lattice spacing from potassium to vanadium, followed by the less rapid fall and eventual increase which is shown in Fig. 117. This point is dealt with in the later theories described below.

(3) *Specific Heat.*

The total specific heat of a metal may be regarded as the sum of the normal specific heat resulting from the thermal vibrations of the atoms, and that due to the valency electrons. We may consider first the normal specific heat due to the atomic vibrations. If U is the internal energy associated with the atomic vibrations, the resulting normal specific heat at constant volume is defined by the relation $c_v = \frac{dU}{d\theta}$ where θ is the temperature on the absolute scale. If a crystal consists of N atoms held together by elastic forces, the lattice possesses $3N$ vibrational degrees * of freedom, and we may say that there are $3N$ independent normal modes of vibration. These normal modes may be regarded as having frequencies $\nu_1, \nu_2, \nu_3 \ldots$ and the actual condition of the crystal results from the super-position of these $3N$ frequencies, each having an amplitude which depends on the temperature. As the temperature falls, the amplitude and hence the energies of the vibration diminish, and according to the quantum theory, the energy associated with a vibration of frequency ν is :

$$\tfrac{1}{2} h\nu + \frac{h\nu}{e^{\frac{h\nu}{k\theta}} - 1},$$

where h is Planck's constant, k is Boltzmann's constant, and θ is the absolute temperature.

In this expression the term $\frac{1}{2}h\nu$ represents the zero point energy, *i.e.*, the energy which an oscillator still retains at the absolute zero. The second term represents the temperature-dependent part of the energy resulting from a vibration of frequency ν. This term is of such a form that as the temperature becomes very low, and $\frac{h\nu}{k\theta}$ becomes very large,

* More strictly $(3N - 6)$, since the solid as a whole has 3 translational and 3 rotational degrees of freedom. In any crystal of normal size, the number 6 is negligible compared with $3N$.

the temperature-dependent part of the energy and its specific heat become very small, and vanish at the absolute zero. The higher the frequency ν, the higher the temperature below which its energy is negligible. It follows, therefore, that as a metal is cooled, the energies associated with the highest frequencies die away most rapidly, and the lower the temperature the more the energy is associated with vibrations of low frequency and hence of long wave-length. The general picture presented is one in which we have at all temperatures a constant term (the zero-point energy) which does not contribute to the specific heat, and an energy term dependent on the temperature. The latter term and the associated specific heat are zero at the absolute zero, and on raising the temperature the vibrational energy increases in such a way that the energy is first associated with the lowest frequencies.

The details of the process depend on the relative numbers of the different frequencies, or in other words on the frequency-distribution curve, or the vibrational spectrum of the crystal structure. Just as we have drawn $N(E)$ curves to show how the electron states are distributed over different ranges of energy, so we may draw frequency-distribution curves showing how the frequencies are distributed over different ranges. Each type of crystal structure gives rise to a characteristic vibrational spectrum just as it gives rise to a characteristic type of $N(E)$ curve. The form of the vibrational spectrum has been calculated for the body-centred cubic structure, but not for the face-centred cubic structure or for more complicated structures, although various simplified two-dimensional models have been dealt with. The details of this work are complicated and lie outside the present book, although reference may be made to a report by Blackman.* For most purposes the problem is drastically simplified, and the first step was taken by Einstein, who assumed that all the atoms vibrated with the same frequency, so that the vibrational spectrum consisted of one single frequency. This was clearly too simple a model, and the next step was taken by Debye, who assumed that the solid crystal could be treated as an elastic continuum. In this case the theory of elasticity indicates that a specimen of definite size and shape can undergo only certain definite vibrations whose frequencies are related to the elastic properties of the material, and depend also on the size and shape,† although the shape has an appreciable effect only on the lowest frequencies. In this case if $N(\nu)$ is the number of frequencies in the range ν and $\nu + d\nu$, it is easy to show that $N(\nu) \propto \nu^2$; the constant of proportionality involves

* M. Blackman, *Ann. Rep. Progress Physics*, 1941, **8**, 11.

† This is the three-dimensional analogue to the tones and overtones of a stretched string.

the velocities of transmission of waves in the solid, and so forms a connecting link between the theory of elasticity and the theory of specific heat. In the case of a true continuum there is no upper limit to the frequency, but in a crystal the atomic structure imposes an upper limit to the frequency, since there is a minimum wave-length of the order of the distance between two atoms. The assumption made by Debye was then that the equations for an elastic continuum could be applied to a crystal, provided that the spectral distribution curve was cut off sharply at a limiting frequency ν_D such that the total number of frequencies is equal to $3N$. This assumption is purely arbitrary, and the theory is a rather illogical mixture of what would be expected for a continuum, and what is required for an actual lattice. It has become increasingly clear that for some problems the Debye theory is too simple, but in many cases it is a justifiable approximation at low temperatures, and it leads to the following conclusions:

(1) If the limiting frequency is ν_D, we may define a characteristic temperature $\bar{\theta}$ by the relation $\bar{\theta} = \frac{h\nu_D}{k}$. In this case the specific heat of all metals should be the same function of $\bar{\theta}$, so that different metals should have the same specific heats if they are compared at temperatures which are the same fraction of the characteristic temperature. This is found to be the case for many cubic metals. For non-cubic metals it is necessary to introduce more than one characteristic temperature because the elastic properties are different in different directions, and similar difficulties are encountered in some cubic metals if these are elastically very anisotropic.

(2) At very low temperatures the theoretical specific heat is proportional to θ^3, and this is in reasonable agreement with the facts for some metals, although really critical tests are difficult to make.

(3) At high temperatures the atomic heat should approach asymptotically to the value $C_v = 3R = 6$ cal. units, in agreement with Dulong and Petit's law. The fact that at very high temperatures the atomic heats exceed this value is partly because the amplitudes of the vibrations become too large for them to be treated as simple harmonic vibrations, and also to the increase of the electronic specific heats referred to below.

Considered empirically the Debye theory has achieved great success, but there is increasing evidence that there are discrepancies between the thermal and elastic data, and it is generally recognized that the use of the continuum hypothesis, although often satisfactory for some low-temperature properties, is too great an approximation.

In an actual metal we have to consider not only the normal atomic

heat resulting from the thermal vibrations, but also that resulting from the electrons. In Part IV (p. 163) we have seen that the specific heat of the degenerate electron gas can be expressed in the form :

$$c_v = \frac{\pi^2 k^2}{2\varepsilon^*} N\theta.$$

we write ε^* for the value of $E_{max.}$ at the absolute zero of temperature, we may define a characteristic temperature, by the relation $\theta_0 = \varepsilon^*/k$, where k is Boltzmann's constant. The specific heat per gram at constant volume may be written in the form :

$$c_v = \frac{\frac{2}{3}\pi^2 k^2 \theta}{\rho} \times N(\varepsilon^*) \quad . \quad . \quad . \quad . \quad . \quad \text{VI (6)}$$

where $N(\varepsilon^*)$ is the density of states at the surface of the Fermi distribution at the absolute zero. In the general case, when the energy and wave number at the bottom of a band are related by the formula $E = \alpha h^2 k^2/2m$, where k is the wave number,†

$$\theta_0 = \frac{\varepsilon^*}{k} = \alpha \frac{h^2}{8mk} \left(\frac{3N}{\pi V}\right)^{\frac{2}{3}} \quad . \quad . \quad . \quad . \quad \text{VI (7)}$$

where N/V is the number of electrons per unit volume. For free electrons $\alpha = 1$, and the specific heat may be written :

$$c_v = \frac{1}{2}\pi^2 nk \frac{\theta}{\theta_0} \quad . \quad . \quad . \quad . \quad . \quad \text{VI (8)}$$

where n is the number of electrons per unit mass. In this case θ_0 is of the order 10^4–$10^{5°}$ K., so that at room temperatures the electron gas is almost completely degenerate, and the electronic specific heat is negligible compared with the atomic heat. From equation VI (6) it will be seen that the electronic specific heat increases with $N(\varepsilon^*)$, and is consequently greater for an $N(E)$ curve which is high in the region of the Fermi surface.

The above considerations refer to electron states at the bottom of a band, and we may now consider the position at the head of a band. Fig. 120 shows a hypothetical case in which the occupied states at the absolute zero extend as far as the point ε^*. We have already explained (p. 209) that the $N(E)$ curves at the head of the band are parabolic and are of the form :

$$N(E) \propto \sqrt{E_\omega - E} \quad . \quad . \quad . \quad . \quad . \quad \text{VI (9)}$$

where E_ω is the energy at the head of the band. On raising the temperature from the absolute zero, the sharp edge of the occupied states

† It is common practice to use the same symbol k for the wave number and for Boltzmann's constant. It is only in the present section that any possibility of confusion arises, and a special symbol is used here for the wave number.

at $E = \epsilon^*$ is replaced by a diffuse distribution, and some of the states with $E > \epsilon^*$ are now occupied, whilst some of those for which $E < \epsilon^*$ are no longer fully occupied. It will be seen, therefore, that the effect of rising temperature is to make the *unoccupied states or "holes"* in the band diffuse backwards from the head of the band, towards the region of lower energy, just as, when we deal with the free-electron model, the *occupied states* diffuse outwards towards the region of higher energy. The conclusion reached is, therefore, that when we deal with a metal containing a nearly full band of electrons, the effect of temperature on the electron distribution at the edge of the Fermi surface is expressed by equations similar to those given above, except that unoccupied states or "positive holes" must be substituted for occupied states. In this case, if E_ω is the energy at the head of the band, we may define a characteristic temperature by the relation $k\theta_0' = (E_\omega - \epsilon^*)$, and the electronic specific heat may be written in the form:

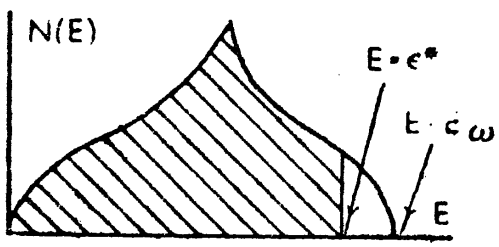


FIG. 120.

$$c_v = \frac{1}{2\alpha}\pi^2 nk\,\frac{\theta}{\theta_0'} \quad . \quad . \quad . \quad . \quad . \quad \text{VI (10)}$$

where n is the number of "positive holes per gram." In the case of nickel, for example, n is equal to 0·6 multiplied by Avogadro's number and divided by the atomic weight, since there are 0·6 positive holes per atom. We have already seen that the $N(E)$ curve for the d-band is very high, and when numerical values are inserted, it is found that θ_0' is of the order of $10^{3°}$ K., so that the positive holes are much less degenerate than free electrons or electrons at a Fermi surface which occurs at the bottom of a band, for which, as stated above, θ_0 is of the order of 10^4–$10^{5°}$ K. It is in this way that the theory of Mott and Jones accounts for the abnormally high specific heat of the transition metals. In the case of the ferromagnetic metals there is a further specific-heat term for the heat required to demagnetize the body.

(4) *Pauling's Theories.*

The next step towards an understanding of the transition metals was taken by Pauling, who discussed the problem from the point of view of the orbital model referred to in Part III. The assumption made by Pauling is that bond formation in the transition elements is due to electrons in s, p, and d-states, and not only to electrons in s-states. The d-orbitals alone are not well suited to bond formation,

but hybridization between *s*, *p*, and *d*-orbitals may lead to very stable bond orbitals, such as those formed in the ferricyanide ions $Fe(CN)_6'''$. The 3*s* and 3*p*-orbitals are too deep down in the atoms to be available for bonding orbitals, and in the elements of the First Long Period there are nine orbitals available for bond-formation, five 3*d*, one 4*s*, and three 4*p* orbitals. From a study of the interatomic distances and other properties, Pauling concludes that 2·44 *d*-orbitals per atom show weak interatomic interactions, and may be regarded as associated

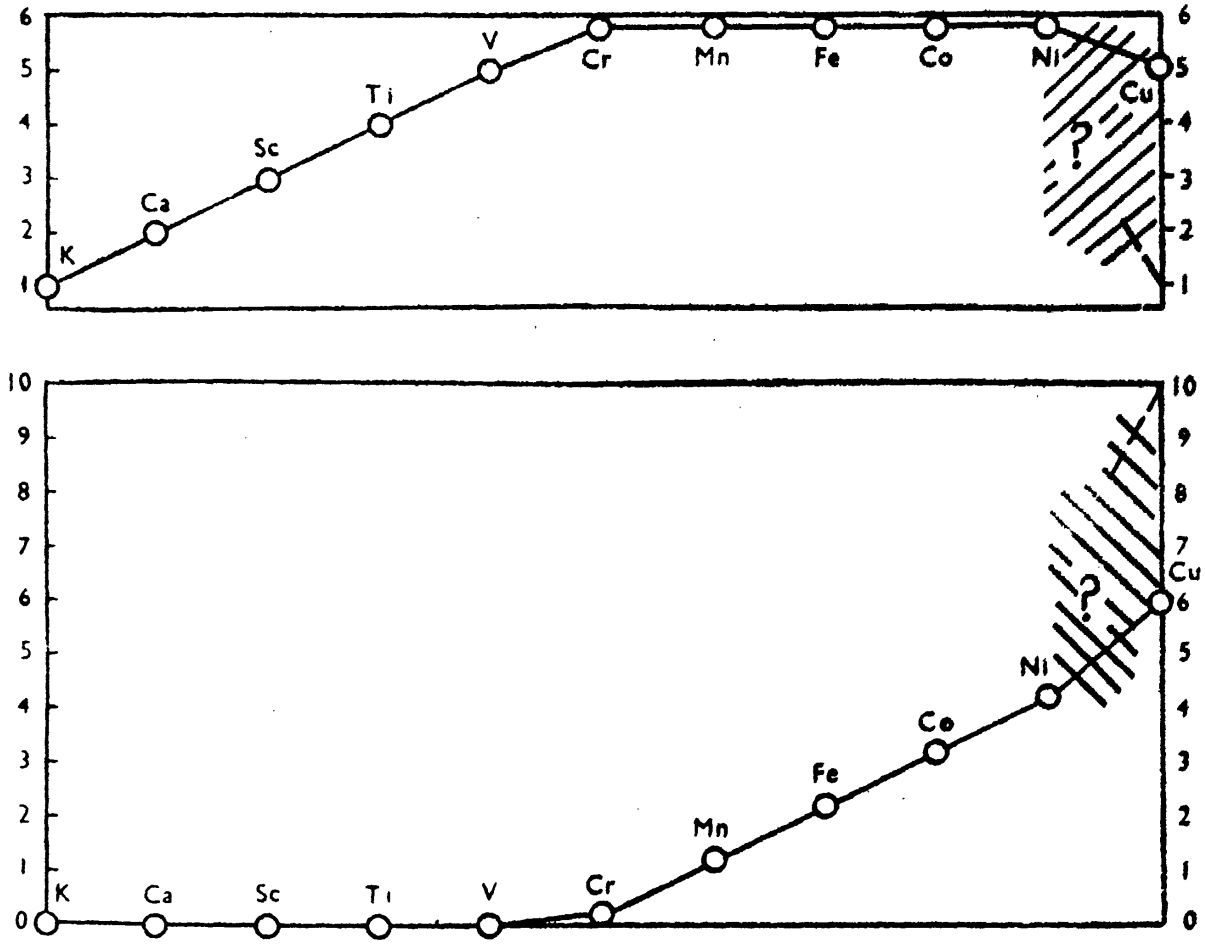


FIG. 121.—(*Above*) Number of Bonding Electrons per Atom (after Pauling). (*Below*) Number of (3*d*) Electrons per Atom in Atomic Orbitals and not Forming Bonds.

with the individual atoms, and so do not form bonds. These *d*-orbitals may be called atomic *d*-orbitals, and in accordance with the general principles (see p. 53) the electrons in the atomic *d*-orbitals tend as far as possible to remain unpaired, and it is the unpaired electrons which give rise to the atomic saturation magnetic moments. The remaining 2·56 *d*-orbitals per atom are available for bond-formation, and may be called bond orbitals, and they hybridize with *s* and *p* valency orbitals to form the metallic bonds.

The picture of the elements of the First Long Period given by Pauling is that from potassium to vanadium, there is a continuous increase of from one to five electrons per atom available and used for bond formation.* This agrees with the rapid decrease in atomic diameter, and with the fact that vanadium is only weakly paramagnetic; if only the two *s*-orbitals were used for bond-formation, as in the theory of Mott and Jones, the core of the atom would have an incomplete *d*-shell, and would be strongly paramagnetic or even ferromagnetic. In chromium, Pauling considers that 5·78 electrons per atom are used in bond-formation, and that the remaining 0·22 electrons per atom enter the atomic 3*d*-orbitals, and from this stage onwards he considers the number of bonding electrons as approximately constant. The number of electrons, N_a, to be accommodated in the atomic *d*-orbitals will then be as follows:

Cr.	Mn.	Fe.	Co.	Ni.
0·22	1·22	2·22	3·22	4·22

The model assumes that there are 2·44 atomic *d*-orbitals per atom, and since the electrons in these remain unpaired as long as possible, the saturation magnetic moment in Bohr magnetons will be N_a for chromium, manganese, and iron. In cobalt and nickel some of the electrons in

TABLE VI.—*Predicted and Observed Values of Saturation Magnetic Moments.*

Element.	Cr.	Mn.	Fe.	Co.	Ni.	Cu.
Predicted saturation Magnetic moment in Bohr magnetons.	0·22	1·22	2·22	1·66	0·66	*d*-shell filled
Observed value . .	...	...	2·22	1·71	0·61	...

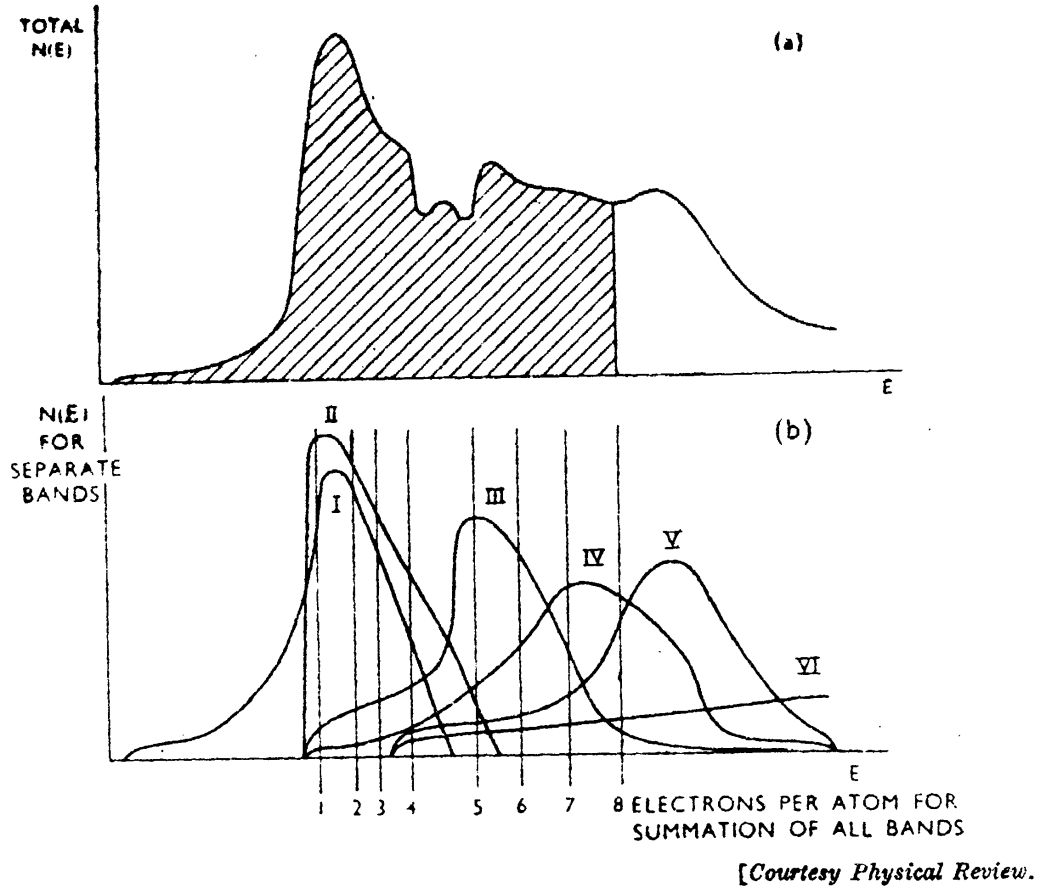
the atomic *d*-orbitals will be paired, and the saturation magnetic moment will be given by $(4{\cdot}88 - N_a)$. The predicted and observed values are shown in Table VI. The hypothesis that there are 2·44 atomic *d*-orbitals was based on the fact that the maximum saturation moment is given by an alloy of iron and cobalt. Pauling carries his hypothesis further, and assumes that the *d*-orbitals play a considerable part in the cohesion of copper and zinc, but this extension of the theory has not been given any quantitative support. In general it may be said that Pauling's hypothesis that the *d*-electrons play an important

* The idea that the number of electrons used in bond-formation increased from one to five on passing from potassium to vanadium was first put forward by Hume-Rothery in 1931, but the details suggested were wrong, owing to attempts made to ascribe a definite electronic state to the atoms in the metals.

part in the cohesion of the transition elements is undoubtedly correct, and for the transition elements of the earlier groups his viewpoint is more satisfactory than that of Mott and Jones. For the last transition element of each Long Period, and for copper, silver, and gold, Pauling's hypothesis probably over-estimates the part played by the *d*-electrons in the cohesion process, and it may be said that if Mott and Jones tend to under-estimate the effect of the *d*-electrons on cohesion, Pauling tends to over-estimate it for the last transition elements and the elements which immediately follow them.

(5) *Electron Bands in Iron.*

Our understanding of the transition elements has been carried considerably further by the work of Manning and of Greene and Manning, who have calculated the form of the electron bands in body-

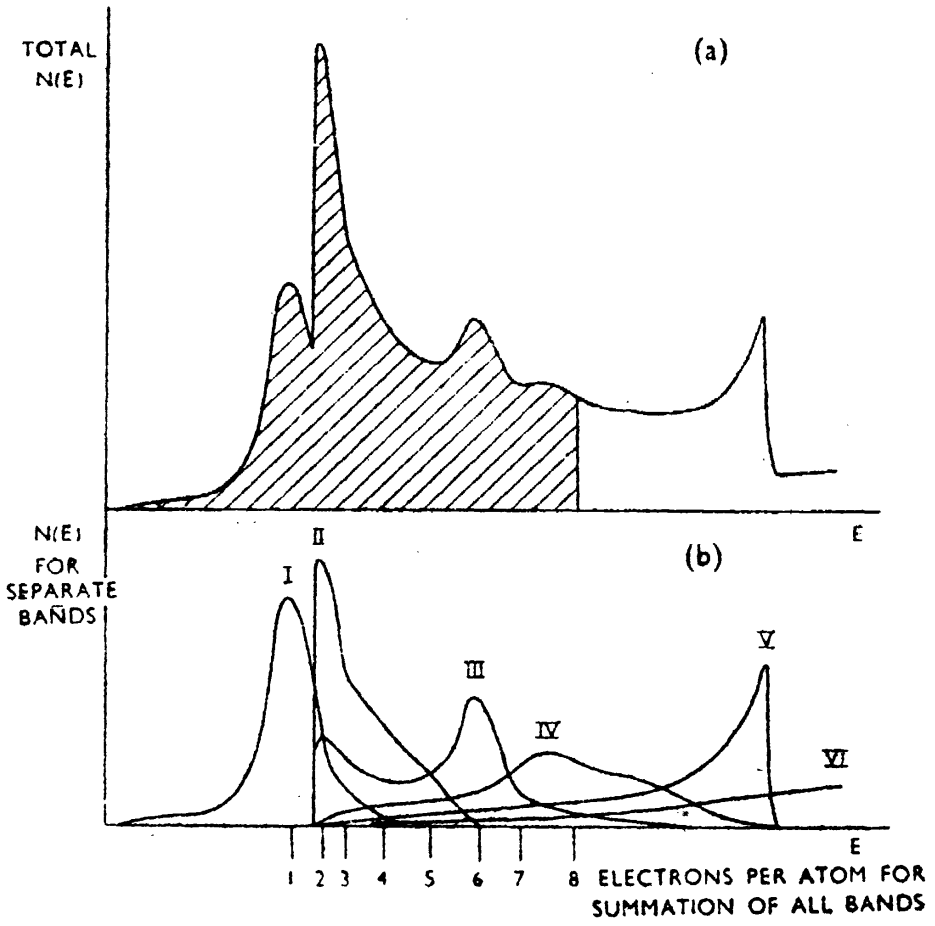


[*Courtesy Physical Review.*

FIG. 122.—$N(E)$ Curves for Body-Centred Cubic Iron.

centred cubic and face-centred cubic iron. In body-centred cubic iron the electron states may be regarded as occupying six bands, and the $N(E)$ curves for these are shown in Fig. 122(*b*), whilst Fig. 122(*a*) shows the total $N(E)$ curve. The wide and low band, No. VI, is composed mainly of 4*s* states, and corresponds with the *s*-band of the

model of Mott and Jones. It is this band which is responsible for most of the electrical conductivity. The remaining bands, I–V, are composed of a mixture of 4*s*, 4*p*, and 3*d* states, and in iron the first two of these are completely filled, and so contribute nothing to the conductivity or to the ferromagnetic properties. From what follows below, it appears probable that the electrons in bands I and II form electron clouds which are concentrated near to the ions, and which give rise to repulsive rather than to attractive forces. The bands



[*Courtesy Physical Review.*

FIG. 123.—$N(E)$ Curves for Face-Centred Cubic Iron.

numbered III, IV, and V are incompletely filled, and are important in connection with the ferromagnetism.

Fig. 123 shows the corresponding curves for face-centred cubic iron, from which it will be seen that although the details are profoundly different, the general position is very much the same. There are again two completely filled bands, I and II, three incompletely filled bands, III, IV, and V, and a wide, low band, VI, composed mainly of *s*-states and responsible for most of the electrical conductivity.

The curves given by Manning refer to iron, but they are of great

interest in connection with the problem of the transition metals in general. As a very rough approximation we may assume that the general nature of the curves in Figs. 122(*b*) and 123(*b*) is preserved for the one or two elements on either side of iron in the Periodic Table. In these figures we have marked the positions corresponding to 6, 7, and 8 electrons per atom, respectively, these points having been obtained graphically from the data given by Manning and by Manning and Greene. In both face-centred and body-centred cubic structures, the energies corresponding with 10 electrons per atom come just before bands I–V are filled, in agreement with the fact that nickel has a few holes in the *d*-shell. On the side of lower valency it will be seen that at 6 electrons per atom, bands I and II are filled in the body-centred cubic structure and almost filled in the face-centred cube. This clearly suggests that the change in the direction of the atomic-diameter/atomic-number curve which occurs between vanadium and chromium in Fig. 117, is the result of the complete filling of bands I and II of Manning's calculations, and that after these bands are full their electrons become concentrated round the nuclei and so give rise to repulsion rather than to attraction. As we shall see later (p. 277), one of the criteria for ferromagnetism is the existence of incompletely filled shells of electrons which do not overlap too greatly in real space, and from this point of view we may interpret the characteristics of the elements of the First Long Period as follows.

Potassium is a typical alkali metal with a half-filled Brillouin zone, and is of a very open type (see Chapter XXVI). On passing to calcium there is a slight overlap into a second zone (see p. 241), the electron states in the first zone being derived from the 4*s* and 4*p*-states of the free atom, and those of the second zone involving also 3*d*-states. On passing from calcium to vanadium there is a continual increase in the number of electrons concerned in the cohesive process, and as suggested by Pauling, electrons in hybridized 3*d*-states take part in the cohesive process, with a resulting increase in cohesion and decrease in atomic diameter. The electron clouds of these *d*-states are still comparatively large, and overlap considerably, so that ferromagnetism is not shown, and this stage in the process results in the filling up of bands I and II indicated by Manning's calculations (Fig. 123). On reaching chromium, bands I and II are filled, and the electron clouds corresponding to these states become more densely packed round the nuclei, and so begin to give rise to repulsion rather than to attraction. The decrease in atomic diameter then becomes less marked, but the cohesion still remains high, because the additional electrons can enter bands III, IV, and V, where hybridized *d*-orbitals give strong binding. At

first, the electron clouds of these bands in real space overlap too much for ferromagnetism to be shown, but with increasing atomic number they contract until the critical point is reached in the region iron, cobalt, and nickel, and ferromagnetism is shown. On passing from iron and cobalt to nickel, the cohesion becomes weaker, and the atomic diameter becomes greater, until when copper is reached and the *d*-shell is complete, the *d*-electrons play a smaller part in the cohesion process. On passing to zinc, the *d*-shell contracts markedly as described in Chapter XXVIII (p. 249), and the *d*-electrons play little or no part in the cohesive process, with the result that the binding becomes much weaker, and the melting point falls to 419° C.

As previously explained (p. 102), gallium has an abnormal crystal structure, the reason for which is not understood, although the Brillouin zone has been investigated by Raynor.* On passing to the succeeding elements germanium, arsenic, selenium, and bromine, the electronegative nature of the element becomes more pronounced, and the crystal structures obey the "$(8 - N)$" Rule (p. 99). We have already explained that the diamond type of structure gives rise to a zone which contains exactly four electrons per atom, and that the insulating properties of the diamond were the result of the zone being completely filled. Germanium has the same structure, but is a semi-conductor, and presumably the energy gap between the zone which contains four electrons per atom and the next higher zone is much smaller than in the diamond, with the result that as the temperature rises above the absolute zero, some electrons are thermally excited into the next zone, and so create a conductivity. Alternatively the conductivity may be due to the presence of impurities as described on p. 206. As explained before, the co-valency and Brillouin-zone theories of the diamond structure are complementary, and each expresses part of the truth. In the same way the crystal structure of selenium, which is quite properly looked on as a co-valency $(8 - N)$-rule structure, has been shown to give rise to a zone containing six electrons per atom, and thermal excitation to the next zone or the presence of impurities are regarded as responsible for the properties of a semi-conductor. The crystal structure formed by arsenic, antimony, and bismuth gives rise to a zone containing five electrons per atom, and the case of bismuth has been examined in great detail by H. Jones, who shows that many of the properties can be accounted for if there is a slight overlap from this zone, so that the outer zone contains a very few electrons, and there are a corresponding number of holes in the main zone. The properties of arsenic have not been examined in such detail, and since metallic arsenic is of little practical

* *Phil. Mag.*, 1941, [vii], **31**, 139.

value, we shall not refer to it here, although the diamagnetism of bismuth is referred to later (p. 282).

REFERENCES AND SUGGESTIONS FOR FURTHER READING.

General Theory of Transition Elements.

N. F. Mott and H. Jones, "The Theory of the Properties of Metals and Alloys." Oxford: **1936** (Clarendon Press).

F. Seitz, "The Modern Theory of Solids." New York: **1940** (McGraw-Hill Book Co., Inc.).

L. Pauling, *Phys. Rev.*, 1938, [ii], **54**, 899.

W. Hume-Rothery, *J. Inst. Metals*, 1944, **70**, 229.

Electron Bands in Iron.

M. F. Manning, *Phys. Rev.*, 1943, [ii], **63**, 190.

J. B. Greene and M. F. Manning, *ibid.*, p. 203.

Electronic Theory of Bismuth Crystals.

H. Jones, *Proc. Roy. Soc.*, 1934, [A], **144**, 225; **147**, 396.

Chapter XXX.—Some Magnetic Properties.

In the previous Chapter we have referred to the appearance of ferromagnetic properties in the elements iron, cobalt, and nickel, and we may now describe briefly the theories of this subject. The phenomenon of ferromagnetism has been known for a very long time, but it was not until the middle of the 19th century that it was shown conclusively by Faraday that other substances showed magnetic properties, and that in general three classes could be distinguished. If a specimen, in the form of a rod, is placed in a magnetic field, the substance concerned is said to be *diamagnetic* if the rod tends to set itself at right angles to the field, and *paramagnetic* if it tends to set itself parallel to the field. Diamagnetic substances are repelled by a magnet, whilst paramagnetics are attracted. In diamagnetic and paramagnetic substances, the magnetic effects are only shown in the presence of an external field, but the third class of *ferromagnetic* substances may become permanently magnetized, although the magnetism may be destroyed by heating to a sufficiently high temperature, and above this temperature they become paramagnetic. The magnetic susceptibility of diamagnetic substances * is negative, and that of paramagnetic substances is positive. The susceptibility of ferromagnetic substances is, of course, positive, and is very large numerically, until the field becomes so strong that the specimen approaches saturation. The majority of metals and alloys are weakly paramagnetic or weakly diamagnetic, and as will be seen from Table VII, the mass susceptibilities are of the order 10^{-6}–10^{-7}, so that the gram-atomic susceptibilities are of the order 10^{-5}–10^{-6}. The metals of the Rare Earth Group are very much more strongly paramagnetic, with gram-atomic susceptibilities of the order 10^{-2}, and a few transition elements such as palladium and manganese are distinctly more paramagnetic than the ordinary metals, whilst antimony and bismuth have rather larger diamagnetic susceptibilities. Ferromagnetism is restricted to the elements iron, cobalt, and nickel in the First Long Period, whilst gadolinium in the Rare Earth Group is also ferromagnetic at very low temperatures. In general,

* The susceptibility κ is a means of representing the magnetizability of a substance, and is defined so that if the intensity of magnetization is I in a magnetizing field of strength H, then $I = \kappa H$. When κ is positive the substance is paramagnetic, and when negative the substance is diamagnetic.

The intensity of magnetization refers to unit volume, and the mass susceptibility χ is equal to $\frac{\kappa}{\rho}$, where ρ is the density, whilst the gram-atomic susceptibility is equal to the mass susceptibility multiplied by the atomic weight.

however, there is a fairly clear division of the metallic elements into what might be called normal metals (*i.e.*, weak para- or diamagnetism), strongly paramagnetic metals (the Rare Earths), and ferromagnetics. Since ferromagnetic substances become paramagnetic at a sufficiently high temperature, the facts suggest strongly that ferromagnetism is

TABLE VII.—*Magnetic Susceptibilities of the Elements.*

(Mass Susceptibilities.)

	$\chi \times 10^6$.		$\chi \times 10^6$.		$\chi \times 10^6$.		$\chi \times 10^6$.
H 1	− 1·97	Cu 29	−0·086	Cs 55	− 0·22	Au 79	−0·15
He 2	− 0·47	Zn 30	−0·157	Ba 56	+ 0·9	Hg 80	−0·168
		Ga 31	−0·24	La 57	+ 1·04	Tl 81	−0·24
Li 3	+ 0·50	Ge 32	−0·12	Ce 58	+15·0	Pb 82	−0·12
Be 4	− 1·00	As 33	−0·31	Pr 59	+25·0	Bi 83	−1·35
B 5	− 0·69	Se 34	−0·32	Nd 60	+36·0	Po 84	...
C 6	− 0·49	Br 35	−0·39	Il 61	...	— 85	...
N 7	− 0·8	Kr 36	...	Sm 62	...	Rn 86	...
O 8	+106·2			Eu 63	+22·0		
F 9	...	Rb 37	+0·21	Gd 64	Ferro.	— 87	...
Ne 10	− 0·33	Sr 38	−0·20	Tb 65	...	Ra 88	...
		Y 39	+5·3	Dy 66	...	Ac 89	...
Na 11	+ 0·51	Zr 40	−0·45	Ho 67	...	Th 90	+0·11
Mg 12	+ 0·55	Cb 41	+1·5	Er 68	...	Pa 91	+2·6
Al 13	+ 0·65	Mo 42	+0·04	Tu 69	...	U 92	...
Si 14	− 0·13	Ma 43	...	Yb 70	...		
P 15	− 0·90	Ru 44	+0·50				
S 16	− 0·49	Rh 45	+1·11	Lu 71	...		
Cl 17	− 0·57?	Pd 46	+5·4	Hf 72	...		
A 18	− 0·45			Ta 73	+ 0·87		
		Ag 47	−0·20	W 74	+ 0·28		
K 19	+ 0·52	Cd 48	−0·18	Re 75	...		
Ca 20	+ 1·10	In 49	−0·11	Os 76	+ 0·05		
Sc 21	...	Sn 50	−0·25	Ir 77	+ 0·15		
Ti 22	+ 1·25	Sb 51	−0·87	Pt 78	+ 1·10		
V 23	+ 1·4	Te 52	−0·31				
Cr 24	+ 3·08	I 53	−0·36				
Mn 25	+ 11·8	Xe 54	...				
Fe 26	Ferro.						
Co 27	,,						
Ni 28	,,						

either an extreme form of, or closely connected with, paramagnetism, and that diamagnetism is distinct.

Most theories of ferromagnetism involve the assumption that ferromagnetic substances contain a number of elementary magnets, and that the magnetic state corresponds with these elementary magnets all taking up the same orientation. The general characteristics of the phenomena can be explained if the ordered or orientated state is the result of a "co-operative process" in which the energy required to change the orientation of one elementary magnet increases with the

perfection of the orientation of all the other elementary magnets. If, for example, all the elementary magnets are pointing in the same direction, then a change in the orientation of any one elementary magnet will be opposed by the order of the whole assembly,* whereas the less perfect the order of the assembly, the smaller will be the average restraining force exerted on any one elementary magnet. In this way it is possible to show that on raising the temperature, the magnetism will be destroyed, at first slowly, and then with a sudden rush, over a comparatively narrow range of temperature, at the so-called *Curie Point.*† Above the Curie point, the substance becomes paramagnetic, and its susceptibility varies with the temperature, according to a relation of the type ‡ :

$$\chi = \frac{C}{\theta - \bar{\theta}_0},$$

where θ is the temperature concerned, and $\bar{\theta}_0$ the temperature of the Curie point. Many ordinary paramagnetic substances (*i.e.*, those which are paramagnetic and do not exhibit ferromagnetism at a low temperature) have susceptibilities which vary with the temperature according to a relation of the type :

$$\chi = \frac{C}{\theta + A}$$

and if we write $-A = \bar{\theta}_0$, then $\bar{\theta}_0$ may be called the negative Curie temperature of the material.

Many considerations led to the conclusion that the elementary magnets must be either electrons revolving in orbits, or the spinning electrons which had been found to explain the finer details of atomic structure. In either case, the ferromagnetic body would contain something which was revolving, and the known properties of gyroscopes led to the prediction of the various gyromagnetic phenomena, in which, according to the nature of the experiment,§ rotation of a ferromagnetic substance produces magnetization, or alternatively the sudden magnetization of the substance tends to produce rotation. If we use the symbol ρ to denote the *gyromagnetic ratio, i.e.*, the ratio of the angular momentum and the magnetic moment of the elementary

* The effect of any one elementary magnet is, of course, mainly due to its immediate neighbours, and to a lesser extent by those further away.

† The general nature of the process is very like that of the destruction of the long-range order of a superlattice in a solid solution.

‡ It should be noted that the $\bar{\theta}_0$ in this equation, the paramagnetic Curie point, is not really exactly the same as the ferromagnetic Curie point, at which the ferromagnetism disappears, but for the present purpose this difference may be ignored.

§ An interesting account is given in "Modern Magnetism," by L. F. Bates. Cambridge: 1939 (University Press).

magnetic gyrostat, it can be shown that for a spinning electron $\rho = m/e$, whilst for an electron in a circular orbit $\rho = 2m/e$. In the general case, $\rho = 1/g \cdot 2m/e$, where g is the so-called *Landé splitting factor*, and equals 2 for a spinning electron and 1 for orbital motion. Experiment then showed that for ferromagnetics for which reliable results could be obtained, g was equal to 2, and it is therefore concluded that in ferromagnetics the elementary magnets are spinning electrons, and it is assumed that the same applies to the strongly paramagnetic elements.

The question then arises as to why the elementary magnets should set themselves parallel in some instances and not in others. We have seen in the general theory of Parts IV and V that the electrons at the absolute zero occupy the $N/2$ lowest energy states, each state containing two electrons of opposite spins. Since each electron state cannot contain more than one electron of a given spin, it is clear that any preponderance of electrons of a given spin must increase the Fermi energy, and ferromagnetism can only exist if some other factor lowers the energy. The energy process responsible for the stabilization of the ferromagnetic state is the exchange or interchange energy to which reference was made in connection with the structure of the hydrogen molecule (Part III, p. 131). In the hydrogen molecule we saw that the exchange integral was negative, and the most stable state was that in which the two electrons had opposite spins, and thus produced a normal co-valent linkage. In some cases, however, the exchange integral is positive, and then the ferromagnetic state may be the stable condition. From this point of view, the following factors may be regarded as important in determining whether ferromagnetism is shown :

(1) The atoms must have an incomplete shell of electrons.

(2) The incomplete shell must have a relatively low electron cloud density near the nucleus. This means that the second quantum number l must be large, and in practice only d and f sub-groups have to be considered.

(3) The atoms must not be too close together or the electron clouds overlap so greatly that the exchange integral is negative, and normal cohesion, with electron pairs of opposite spins, is encountered.

(4) The atoms must not be too far apart, or the exchange integral becomes very small, and the resultant energy term is too small to stabilize the ferromagnetic state. If we denote by D the ratio of the distance between two atoms in a crystal and the " diameter of the orbits " of the overlapping electron shell,* then the relation between

* The expression " diameter of the orbit " is used to denote twice the distance from the nucleus to the point at which the outer part of the electron shell concerned has its maximum electron cloud density.

the exchange integral A and the value of D is of the type shown in Fig. 124. The ferromagnetic elements iron, nickel, and cobalt possess values of D corresponding to the part of the curve where A is relatively large and positive. The dependence of ferromagnetism on a critical value of D is well shown by the fact that, although manganese is not ferromagnetic (because the atoms are too close together), some compounds of manganese are ferromagnetic. Thus one of the manganese nitrides is ferromagnetic, and it has been suggested that this is the result of the manganese atoms being pushed apart by the atoms of nitrogen which exist in interstitial solid solution. The same explanation may account for the ferromagnetism of the Heusler alloys, which consist of copper, manganese, and aluminium in proportions approximating to the composition Cu_2AlMn, whilst ferromagnetism is also shown by some alloys of chromium with tellurium or platinum. The

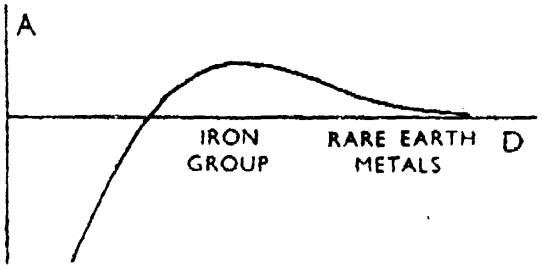


FIG. 124.—In this diagram D is the ratio of the distance between two atoms to the "diameter" of the incompletely filled shell of electrons. If D is small, the exchange integral A is negative, and normal cohesion with electron pairs of opposite spin is obtained. If D is very large, the exchange integral becomes too small to have any appreciable effect. With a critical value of D, the exchange integral is positive and may be large enough to produce ferromagnetism.

general conclusion to be drawn from these considerations is that new ferromagnetic alloys would probably be found if transition elements of Groups VI–VIII were alloyed in such a way as to obtain crystal structures with suitable interatomic distances. It should be noted that if the interatomic distances in the crystal of an element correspond with a point to the left of the maximum on the curve, then compression of the metal decreases the value of A, and so decreases the magnetization. Conversely, destruction of the magnetization tends to produce a contraction, and it is thought that the low coefficient of expansion of alloys such as Invar is due to the alloy corresponding to a point to the left of the maximum in Fig. 124, so that the normal thermal expansion is counteracted by a contraction due to the destruction of the magnetization. The opposite effect is shown by substances which lie to the right of the maximum of Fig. 124.

Since the theories we have described regard the elementary magnets

as consisting of spinning electrons in incompletely filled shells, it is natural to identify the saturation moment at low temperatures * with the number of holes in the *d*-shells in the atoms.† For this purpose the saturation moment must be expressed in Bohr magnetons per atom, and the fact that the observed numbers are not whole numbers implies that on the average a certain fraction of the atoms have a complete *d*-shell and the remainder one, or more probably two (see p. 261), missing electrons. This point of view implies, of course, that we associate the electrons with individual atoms, but this does not imply that a given atom is permanently connected with a given number of electrons. We should say rather that there is a certain probability of an atom having an incomplete *d*-shell with a magnetic moment, and this " hole " in the *d*-shell moves through the lattice, and in the " spin-wave " theory of Bloch the motion of the hole in the *d*-shell is associated with a ϕ wave (= spin-wave) in the same way that the motion of a free electron is associated with a Ψ wave. Just as $\psi^2 d\tau$ is the probability of finding an electron in the volume element $d\tau$ so $\phi^2 d\tau$ is the probability of finding a hole in the *d*-shell in the volume element $d\tau$; in the latter case $d\tau$ should be larger than an atom. The spin-wave can then be associated with a momentum, a kinetic energy, and a velocity, but the details of this theory are too mathematical for the present book.

The above description indicates the reasons for the stability of the ferromagnetic state, but it does not explain why ferromagnetic substances are often found in an apparently unmagnetized condition at temperatures below the Curie point. The first suggested explanation of this was that the substance consisted of a number of crystals, each magnetized in one direction, but with their orientation distributed at random, so that there was no resultant magnetic moment. This explanation was disproved by the discovery that large single crystals of iron or its alloys could also be obtained in the unmagnetized state. The view now accepted is that a single crystal consists of a number of domains, each magnetized in one direction, and that in the non-

* At low temperatures in a strong field, all the elementary magnets point in the same direction. For the relation between this saturation intensity and the results of observations at higher temperatures, reference may be made to " Magnetism and Matter," by E. C. Stoner, London: **1934** (Methuen & Co., Ltd.), and " Modern Magnetism," by L. F. Bates, Cambridge : **1939** (University Press).

† This description is in terms of the older theories. If Pauling's views are accepted, the expression " holes in the *d*-shells " should be replaced by " the number of unpaired electron spins in the atomic *d*-orbitals." For cobalt and nickel the numbers of holes in the *d*-shells are the same as the numbers of unpaired spins in the atomic *d*-orbitals, but for the earlier elements this is not so, because Pauling's theory (p. 268) assumes that there are only 2·44 atomic *d*-orbitals per atom.

magnetic state the effects in the different directions neutralize one another, so that there is no resultant magnetic moment, although the application of an external field causes the different domains to be magnetized in the same direction, with the production of a resultant moment which may be retained as a permanent magnetization when the external field is withdrawn. The existence of these domains has been revealed by the formation of definite patterns when the surface of a ferromagnetic crystal is covered with a suspension of a magnetic oxide of iron. Some of the patterns studied in the early history of the subject were undoubtedly influenced by the straining of the surface of the crystal during the polishing operation, but later and more careful work has avoided this defect, and the existence of magnetic domains in ferromagnetics is now generally accepted.

In Chapter XXII we have seen that the simple free-electron theory of metals indicates a small paramagnetism which is almost independent of the temperature, and a diamagnetism which in the simplest approximation is one-third of the paramagnetism, so that the resultant effect of the free-electron gas is slightly paramagnetic. In the more complete theories the position is very much more complicated, and a large number of factors have to be considered.

In the first place when the results of the calculations are compared with the observed values,* an allowance must always be made for the effect of the ions. Ions with complete outer groups of 8, or 18, electrons are diamagnetic, and their susceptibilities are of the order 10^{-6}, and hence are roughly of the same magnitude as the temperature-independent paramagnetism predicted by the free-electron theory. The fact that one metal is weakly diamagnetic and another weakly paramagnetic does not therefore necessarily indicate any essential difference between the electronic structures of the two metals, but may simply be the result of the diamagnetic contributions due to the ions. Comparison between the observed results and those calculated by the free-electron theory, and corrected for the effects of the ions, is really only justified for the alkali metals, and the general conclusion is that, except perhaps for lithium, the observed paramagnetism is somewhat greater than that calculated.†

When the previous theory (Chapter XXII) of weak spin paramagnetism is examined more carefully, it will be seen that it involves the assumption that there are unoccupied energy states which the electrons can enter when the external field is applied. It follows, therefore, that

* Great care is, of course, necessary to ensure that the observed values are not invalidated by the presence of ferromagnetic impurities.

† Thus rubidium and cæsium are not slightly diamagnetic, according to the calculations, but are actually slightly paramagnetic.

this type of paramagnetism is not to be expected for insulators, which are full zone structures with an energy gap between the occupied and the next higher zone.

In the case of a nearly empty zone for which $N(E) = C\sqrt{E - E_0}$, where E_0 is the energy at the bottom of the zone, the equation IV (35) of the free electron theory still applies, and may be written in the form :

$$\kappa = \frac{3}{2}\frac{N\mu^2}{k\bar{\theta}_0}\left[1 - \frac{\pi^2}{12}\left(\frac{\theta}{\bar{\theta}_0}\right)^2\right] \quad . \quad . \quad . \quad . \quad \text{VI (11)}$$

where the temperature $\bar{\theta}_0$ is defined as before by the relation $k\bar{\theta}_0 = \epsilon^*$, and N is the number of electrons per unit volume. In this case $\bar{\theta}_0$ is very large, and at room temperatures κ is almost independent of temperature. If we consider the case where $\theta/\bar{\theta}_0$ is large, the variation of κ with temperature is given by :

$$\kappa = \frac{N\mu^2}{k\theta}\left[1 - \frac{2}{3\sqrt{2\pi}}\left(\frac{\bar{\theta}_0}{\theta}\right)^{\frac{3}{2}}\right] \quad . \quad . \quad . \quad . \quad \text{VI (12)}$$

These equations also apply to the condition of affairs in an almost full band, where if E_ω is the energy at the head of a band, $N(E) \propto \sqrt{E_\omega - E}$. In this case N is the number of unoccupied states or positive holes per unit volume, and $\bar{\theta}_0$ is defined by $k\bar{\theta}_0 = E_\omega - \epsilon^*$. As we have already seen (p. 266) $\bar{\theta}_0$ for the positive holes is much smaller than $\bar{\theta}_0$ for the degenerate electron gas.

The weak spin paramagnetism of the conduction electrons referred to above is always accompanied by a diamagnetic effect. In the free-electron theory, this diamagnetic susceptibility is one-third that of the paramagnetic susceptibility, but this simple relation no longer holds for electrons in a periodic field. The subject is very complicated, but the theory works out in such a way that the diamagnetism becomes greater when the effective electronic mass m is very small. As we have seen before, m^* is given by :

$$m^* = \frac{h^2}{4\pi^2} \cdot \frac{1}{\dfrac{d^2E}{dk^2}}.$$

where k is the wave number.†

In general for a given zone, $\dfrac{d^2E}{dk^2}$ is greatest, and hence the effective electronic mass is least, at the bottom of a zone, and an abnormally large diamagnetism is to be expected if there is a small overlap into a

† The symbol k is again used to distinguish the wave number from the k of Boltzmann's constant (cf. p. 265).

zone for which $\frac{d^2E}{dk^2}$ is very large at the bottom of the zone into which the overlap occurs. This effect has been worked out in great detail by H. Jones for the case of bismuth, where a number of the magnetic phenomena are explained by assuming that a very small overlap occurs from a zone which, if full, would contain exactly five electrons per atom. This overlap takes place in six directions perpendicular to the axis of the crystal, and the theory explains the diamagnetic anisotropy of single crystals of bismuth.* The phenomena indicate that the number of electrons involved in the overlap is of the order one in every 10^3 or 10^4 atoms, so that the number of electrons concerned is exceedingly small, though this is counterbalanced by the fact that the effective electron mass is also very small. It is to be noted that the abnormal diamagnetism is lost when the solid melts in agreement with the view that the large diamagnetism is a characteristic of the structure, and not of the atom, of bismuth. It is, however, hardly correct to claim this as a conclusive proof of the truth of the zone theories, because a large diamagnetism would also be expected if the crystal structure were regarded as a valency crystal with the bonding electrons moving in relatively large orbits, and here again the effect would be destroyed on melting. As we have already explained, the co-valency and Brillouin-zone theories of the bismuth structure are to be regarded as complementary and not antagonistic.

It remains to consider the metals for which the susceptibility is paramagnetic and abnormally great. The Rare Earth metals belong to this class, and, as already stated, gadolinium is ferromagnetic at very low temperatures. It is thought that other metals of the Rare Earth group may be ferromagnetic with very low Curie points, and that they are structures in which the interatomic distances are greater than those which would correspond with the maximum on the exchange integral curve of Fig. 124. Reference to Table VI will show that apart from the Rare Earth metals, the susceptibilities of the elements of the Long Periods remain small from Group IA to VA, whilst a rather large paramagnetism develops for Groups VIIA and VIII, although ferromagnetism is only shown in the First Long Period (iron, cobalt, and nickel). This rather large paramagnetism of the elements of Groups VIIA and VIIIA is again ascribed to electron spin, the condition being one in which the exchange integral of Fig. 124 is not quite large enough to produce ferromagnetism. We have already explained

* The diamagnetic susceptibility parallel to the principal axis is due to the electrons which have overlapped from the zone which would contain 5 electrons per atom if completely full. The susceptibility perpendicular to the axis is due to the electrons within the zone.

that in the case of nickel, the properties of the alloys confirm the view that there are 0·6 positive holes per atom in the *d*-shell. In the same way the solid solutions of some elements in palladium show properties which vary with the composition in such a way as to suggest that there are about 0·5–0·6 positive holes per atom in the *d*-shell of palladium. The general electronic structure of palladium is therefore not so very different from that of nickel, and the appearance of ferromagnetism in the latter element is the result of the interatomic distances being at the critical value necessary to give a relatively large positive exchange integral, and there is a similar resemblance between the other elements of Group VIII in the different Periods.

APPENDIX.

Note on the Exact Formulation of the Uncertainty Principle of Heisenberg.

Confusion may be caused by the different ways in which the Uncertainty Principle is expressed. For simplicity we may consider the simultaneous position and momentum of an electron in a one-dimensional problem. If the momentum is measured to a certain degree of accuracy, the Principle implies that the position cannot be specified exactly, but involves some uncertainty. There is a probability of finding the electron over a small region, but this region cannot be defined uniquely by sharp boundaries; the region in which there is a probability of finding the electron merges asymptotically into the regions where the probability is vanishingly small. Frenkel ("Wave Mechanics: Elementary") uses the expression "effective uncertainty" to denote the region outside which the probability of finding the electron is negligible. It is in this sense that we have used the expression "uncertainty" in Chapter IV, and following some authors we have written the Uncertainty Principle in the form $\Delta x \Delta p \nless h$. It will be appreciated that the effective uncertainty cannot be defined uniquely, and some authors therefore write the Principle in the form $\Delta x\, \Delta p \sim h$ (*i.e.*, $\Delta x\, \Delta p$ is of the order h).

In the more advanced developments of the subject, the relative probabilities of finding the electron at different places within the region of effective uncertainty are analysed, *i.e.*, the forms of the wave-packets of Chapter VII are examined. It is then possible to define lengths smaller than the effective uncertainty (*i.e.*, smaller than the length of the wave packet) in such a way that the probability of finding the electron within the length concerned is related by a mean or a root mean square relation with the mean value of the x-co-ordinate over the whole region of the wave packet. Some writers use the symbol Δx to denote these lengths, and refer to them as uncertainties, in which case the Principle takes the form $\Delta x\, \Delta p \geqslant \frac{h}{2\pi}$, or $\Delta x\, \Delta p \geqslant \frac{h}{4\pi}$, according to the exact definition used. In these cases the term Δx is precisely defined, but it is perhaps unfortunate to call it an uncertainty in position, because as Δx is shorter than the length of the wave packet, there will be a definite probability of finding the electron outside the region of

uncertainty as thus defined. If the word " uncertainty " is used in its ordinary sense, it undoubtedly implies the " effective uncertainty " in the sense used by Frenkel.

In view of the difficulties in connection with the definition of " uncertainty in position," it is probably better to write the Principle in the form $\Delta x\, \Delta p \sim h$, and to note that the numerical factor by which h is multiplied depends on the definition of uncertainty which is used. Similar considerations apply to uncertainties in momentum, time, energy, &c.

This note has been added just as the first reprint of the book was going to press, and it has been thought better to leave the text untouched in order to ensure that inconsistencies are not introduced between the earlier and later sections.

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